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REDUCTANT GASES FOR FLUE GAS DESULFURIZATION SYSTEMS

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REDUCTANT GASES FOR FLUE GAS DESULFURIZATION SYSTEMS

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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The report gives results of a study of the use of coal or residual-oil gasification to produce a hydrogen/carbon monoxide-rich gas for use as a reductant for regenerable flue gas desulfurization (FGD) processes. Two different reduction systems are considered: one for the type of FGD process that produces a concentrated SO2 stream; the other, for the type that uses a liquid-phase Claus reactor. Detailed data on the composition of the raw gas from several gasifiers are analyzed. To supplement the data on trace constituents in the gas, thermodynamic calculations were made to determine the equilibrium gas-phase concentrations for a typical coal and typical gasification conditions. Mass transfer was calculated to determine the extent to which certain gaseous species could be removed by water-washing of the gas. The effects of the remaining trace constituents on the components of the reduction systems are analyzed. Additional research on trace constituents and their effects are recommended. The capital and operating costs for reductant systems based on gasification of coal and residual oil are estimated and compared with those for reduction systems based on natural gas.

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by

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ABSTRACT

The use of coal or residual oil gasification to produce a hydrogen/carbon monoxide-rich gas for use as a reductant for regenerable flue gas desulfurization (FGD) processes is considered in this study. Two different reduction systems are considered - one for the type of FGD process that produces a concentrated SO_2 stream and one for the type that uses a liquid-phase Claus reactor.

Detailed data on the composition of the raw gas from several gasifiers are analyzed. To supplement the data on trace constituents in the gas, thermodynamic calculations were made to determine the equilibrium gas-phase concentrations for a typical coal and typical gasification conditions. Mass transfer calculations were made to determine the extent to which certain gaseous species could be removed by water washing of the gas. The effects of the remaining trace constituents on the components of the reduction systems are analyzed. Recommendations for additional research on trace constituents and their effects are made.

The capital and operating costs for reduction systems based on gasification of coal and residual oil are estimated and compared with those for reduction systems based on natural gas.

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REDUCTANT GASES FOR FLUE GAS DESULFURIZATION SYSTEMS

by

D. W. Hissong, K. S. Murthy, and A. W. Lemmon, Jr.

1. INTRODUCTION

One of the major environmental challenges facing the United States today is that of reducing the emissions of sulfur oxides from the flue gases of fossil fuel-fired steam electric power plants. Extensive research and development work is in progress on flue gas desulfurization (FGD) processes to accomplish this. Although the most advanced processes are generally of the "throwaway" type which produce an unusable mixture of sulfur compounds,* development work is also in progress on a number of "regenerable" processes which can ultimately produce either elemental sulfur or sulfuric acid as a by product. For many power plants which will have to install flue gas desulfurization systems, elemental sulfur would be the preferred product. Elemental sulfur is desirable because it is a noncorrosive solid which is easily handled, stored, and shipped, and which can be used in a number of industrial operations.

Since the sulfur in flue gas is in the form of sulfur oxides (primarily SO_2), it follows that any flue gas desulfurization system which ultimately produces elemental sulfur must involve some form of reduction. There are a number of ways in which this reduction can be effected, depending on the nature of the flue gas desulfurization process involved. Theoretically, any carbon source, such as coal, coke, petroleum fractions, or natural gas, can be used as the ultimate reducing agent for the SO_2. Conversion of these materials into more reactive forms may be necessary before the actual reduction of the SO_2 takes place. Most of the alternatives currently being proposed for use with regenerable FGD processes involve the use of natural gas as the ultimate reductant. With the current and projected severe shortage of natural gas, it is imperative that alternate sources of reductants be carefully examined. This is the overall objective of this study.

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* The distinction between throwaway and regenerable processes depends upon whether the sulfur specie produced can be utilized profitably.

The specific objectives of this study are to:

(1) Summarize the reduction technology currently being proposed for use with regenerable flue gas desulfurization process that yield elemental sulfur as a product.

(2) Identify various routes by which materials other than natural gas or light petroleum fractions (liquefied petroleum gas or naphtha) can be used as the ultimate reductants in connection with regenerable flue gas desulfurization processes.

(3) Assess the technical and economic feasibility of the most promising routes identified under Objective 2. This will involve estimating the costs of these routes and comparing with the costs of the currently proposed options identified under Objective 1.

(4) Define the needs for additional development studies or demonstration plants to advance these new options toward the point of commercial use.

This study is directed toward fossil-fuel-fired steam-electric power plants in the United States. The objective at these power plants is to remove about 90 percent of the SO_2 from the flue gas and to recover elemental sulfur as the product from this operation. The material used as the reductant for this operation must be coal, coke, petroleum residual oil, or purchased hydrogen sulfide. Any conversions of these reductants to other forms must be done on the premises of the power plant.

2. SUMMARY

This report deals with the production of reductant gases for regenerable flue gas desulfurization processes from materials other than natural gas. The alternative considered in depth is that of gasifying coal or residual oil to produce a hydrogen/carbon monoxide-rich gas which can be used as the reductant. A number of suitable gasification processes are commercially proven and available in this country. The complexity of the reduction system depends largely on the type of flue gas desulfurization process. For the FGD processes that produce a concentrated SO_2 stream, the reduction system will involve three reaction stages with the first reactor containing either the American Smelting and Refining Company (ASARCO) SO_2 reduction catalyst or a cobalt-molybdenum catalyst. The last two reactors will contain conventional Claus catalysts. For the FGD processes that use liquid-phase Claus reactors, the required H_2S can be generated by reducing some of the elemnetal sulfur product with reducing gas from a gasifier.

The raw gas from the gasifier will have to be washed with water to remove ammonia, tar, and particulate matter. Although experimental data in this area are lacking, thermodynamic and mass transfer calculations indicate that water washing should effectively remove these substances and the associated trace elements. The effects of the remaining trace species on most of the FGD process itself will be insignificant because the amounts are very small in comparison to those already entering the FGD process via the flue gas. For a power plant using 3.5 percent sulfur coal, the amount of coal fed to the gasifier to make the reducing gas will be only about 3.6 percent of the amount of coal fed to the power plant boilers. On the other hand, there are portions of some FGD processes which are sufficiently free of trace species that the introduction of such species via the reducing gas could cause difficulties. The effects of trace species on the reduction systems are not well defined. The only known adverse effects are related to ammonia (for vapor-phase Claus catalyst) and COS (for liquid-phase Claus systems), and these species can be removed from the reducing gas. Experimental studies related to trace species in the reducing gas and their effects on the reduction systems are recommended.

The extent to which the reducing gas must be processed to increase its hydrogen content prior to the reduction is not well defined, particularly for the case in which sulfur is to be reduced to produce H_2S. In this case, shifting of carbon monoxide to hydrogen and removal of carbon dioxide may be required. Experimental studies in this area also are recommended.

Reduction systems based on gasification of coal or residual oil will be relatively expensive, at least in comparison with systems based on natural gas. The following cost estimates apply to a 1000-megawatt power plant fired with 3.5 percent sulfur coal. For the FGD processes that produce a concentrated SO_2 stream, the investment (1975) for the reduction system is about \$15 to \$19/kW and the operating cost is 0.77 to 0.92 mills/kwh (for coal at \$22/metric ton). The ranges given cover the range of product gas SO_2 concentrations from such FGD processes and cover gasification with both air and oxygen. These costs (both investment and operating) represent roughly 15 percent of the estimated costs of the FGD process itself.

For the FGD processes that use liquid-phase Claus reactors, the investment for the reduction system is about \$32/kW and the operating cost is 1.13 mills/kW. In this case the gasification must be done with oxygen. These costs are based on the assumption that the reducing gas must be upgraded by CO shifting and CO_2 removal. If such upgrading can be eliminated, the investment would be reduced by about 30 percent. Including the upgrading, the costs of the reduction system represent roughly 30 percent of the estimated costs of the FGD process itself.

A gasifier-based reduction system will increase significantly the complexity of the overall FGD system. On the other hand, there are other possible benefits of such a reduction system. The gasifier could be used to supply some of the energy requirements of the FGD process, such as for stack gas reheating. This energy could be supplied either as excess by-product steam from the gasifier or as excess fuel gas produced.

Purchased H_2S will play only a minor role as a reductant for SO_2 from power plant FGD systems. The use of H_2S will involve almost entirely by-product streams obtained "across the fence" from a source such as an oil refinery or a natural gas processing plant, and geographical considerations will restrict this usage. For a 1000-megawatt power plant fired with 3.5 percent sulfur coal, H_2S can be produced by reducing sulfur with a coal-based reducing gas for \$55-\$64/metric ton H_2S (2.5-2.9¢/lb) when coal costs \$11-\$33/metric ton. Therefore, purchased H_2S would be economical only if the price were lower than this level as applied to the specific situation.

3. FLUE GAS DESULFURIZATION PROCESSES

An analysis of regenerable flue gas desulfurization processes was made in order to:

(1) Identify those processes which could be used in combination with a reduction process to yield elemental sulfur as a product

(2) Examine the compositions of their product gas streams so that appropriate reduction systems could be selected.

Emphasis was placed on processes which are fairly well advanced in their development, although it should be reemphasized that none of these regenerable processes is as advanced as limestone scrubbing, which has been demonstrated in a number of full-scale installations.

A list of flue gas desulfurization processes which can produce elemental sulfur is presented in Table 3-1. These processes have been classified into four groups on the basis of their reduction requirements. The first two groups (Type A and B) will be referred to frequently in this report. The Type A FGD processes are those which produce a concentrated SO_2 stream which must be reduced. The Type B FGD processes require H_2S as a reductant because these processes include liquid-phase Claus plants.

The Westvaco carbon adsorption process is in a category by itself because, although it requires H_2S internally (to reduce the H_2SO_4 adsorbed on the carbon), the H_2S generation step is an integral part of the process. A flow sheet of this process is shown in Figure 3-1. The process requires a reductant such as hydrogen which can be used to reduce sulfur internally to generate the H_2S.

The Atomics International Aqueous Carbonate process is in a separate category in that it inherently fulfills the desired goal of using a "dirty" (sulfur-containing) ultimate reductant, namely, coke or coal. Any Type A FGD process when coupled with Foster Wheeler's RESOX reduction process would also be in this category. The Bergbau-Forschung process is often coupled with the RESOX process.

TABLE 3-1. FLUE GAS DESULFURIZATION PROCESSES WHICH CAN PRODUCE ELEMENTAL SULFUR

Type A - Processes Which Require Reduction of Concentrated SO_2 Streams

1. Very concentrated SO_2 streams containing only SO_2 and H_2O
   - Wellman-Lord - 85% SO_2
   - Shell-UOP CuO - 90% SO_2 with absorber-stripper, 46% without
2. Less concentrated SO_2 streams containing other species
   - Ammonia scrubbing - 27% SO_2 + H_2O, NH_3
   - Magnesia scrubbing - 24% SO_2 + H_2O, N_2, CO_2, O_2
   - Bergbau-Forschung Carbon Adsorption - 23% SO_2 + H_2O, N_2, CO_2

Type B - Processes Which Require H_2S to Reduce SO_2 Liquid Phase

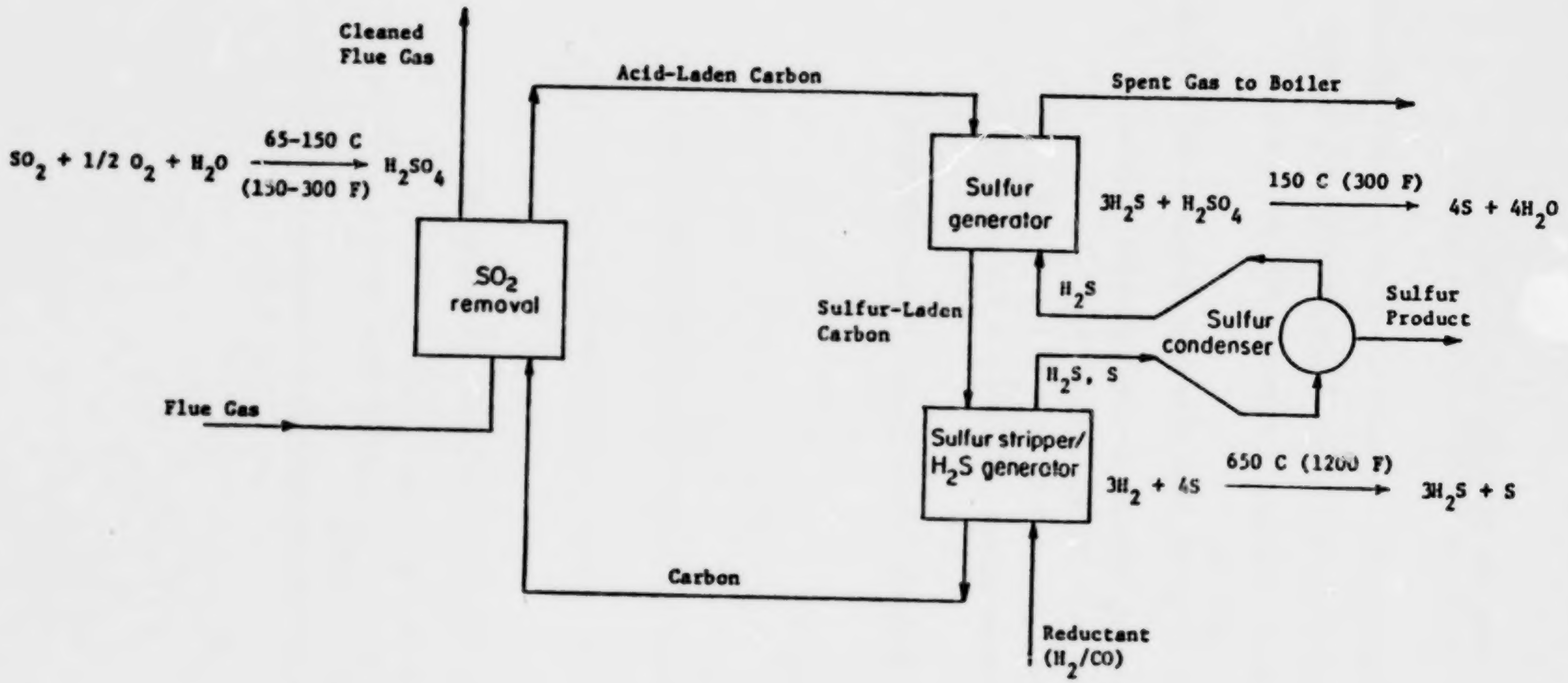
- USBM Citrate
- Stauffer Powerclaus
- IFP-Catalytic NH_3 Scrubbing

Type C - Processes Which Require Reduction of Sulfur Internally to Generate H_2S

- Westvaco Carbon Adsorption - H_2S needed to reduce H_2SO_4 on carbon

Type D - Processes Which Inherently Use a "Dirty" Reductant

- AI Aqueous Carbonate Process - coke
- Any Type A process when coupled with the Foster-Wheeler RESOX reduction process


Cleaned Flue Gas
$SO_2 + 1/2\ O_2 + H_2O \xrightarrow[(150-300\ F)]{65-150\ C} H_2SO_4$
SO_2 removal
Flue Gas
Acid-Laden Carbon
Sulfur generator
Spent Gas to Boiler
$3H_2S + H_2SO_4 \xrightarrow{150\ C\ (300\ F)} 4S + 4H_2O$
H_2S
Sulfur condenser
Sulfur Product
Sulfur-Laden Carbon
H_2S, S
Sulfur stripper/ H_2S generator
$3H_2 + 4S \xrightarrow{650\ C\ (1200\ F)} 3H_2S + S$
Carbon
Reductant (H_2/CO)

Source: "Westvaco SO_2 Recovery Process" brochure, Westvaco Corporation, Charleston, South Carolina.

FIGURE 3-1. SCHEMATIC FLOW SHEET OF WESTVACO FGD PROCESS

For the Type A processes an analysis was made to determine typical compositions of the product gas streams. This involved analyzing literature on the processes and, in some cases, making calculations based on physical properties or reaction stoichiometry. The typical SO_2 concentrations are included in Table 3-1. More information on flue gas desulfurization processes in general and particularly the product gas compositions is presented in Appendix A. Based on the data available, the compositions shown in Table 3-2 were selected as typical for the two classes of Type A FGD processes. These compositions were used in the material balance calculations for the FGD plus reduction systems to be discussed.

There are two Type A processes listed in Table 3-1 for which the product gas contains a species which could be troublesome in the reduction system. In ammonia scrubbing, the residual ammonia in the product gas could act as a poison toward the catalysts used in the reduction system. The effects of ammonia will be further discussed later in this report. In magnesia scrubbing, the oxygen in the product gas (about 4 mole percent) will increase the consumption of the reductant.

TABLE 3-2. TYPICAL COMPOSITIONS OF TYPE A FGD PRODUCT GASES

	Volume Percent in Product Gas from FGD Process	
Specie	Class 1 - Very Concentrated SO_2 Stream	Class 2 - Less Concentrated SO_2 Stream
SO_2	85	25
CO_2		17
N_2		43
H_2O	15	15
	100	100

4. POSSIBLE ROUTES TO ELEMENTAL SULFUR

The various possible routes by which a flue gas desulfurization system can be integrated with a reduction system to yield an elemental sulfur product are considered in this section. At this point no consideration will be given to whether the technology for a given step has been proven or even attempted. The status of this technology will be reviewed in Section 5. The various options will be considered separately for the two types of flue gas desulfurization processes of interest in this study.

4.1 Type A FGD Processes (Those Producing Concentrated SO_2)

The possible routes to elemental sulfur which are within the scope of this study and apply to Type A flue gas desulfurization processes are shown in Figure 4-1. The problem here is one of reducing SO_2 in a relatively concentrated stream to elemental sulfur. The reduction schemes may be classified as being either "direct" or "indirect." In direct reduction, the SO_2 is reduced catalytically to elemental sulfur in one step without going through any other observable oxidation states. Hydrogen, carbon monoxide, and carbon have been studied as reductants for direct reduction. Indirect reduction involves more than one step, with the final step being the reaction of SO_2 with H_2S in a Claus plant to produce elemental sulfur. The H_2S may be obtained by hydrogenation (reduction) of either SO_2 or process-produced elemental sulfur. The H_2S may also be purchased externally. Excluding the external purchase of H_2S, an indirect reduction scheme means that part of the sulfur initially present in the +4 valence state (SO_2) is reduced all the way to the -2 valence state (H_2S) before the desired zero valence state is achieved.

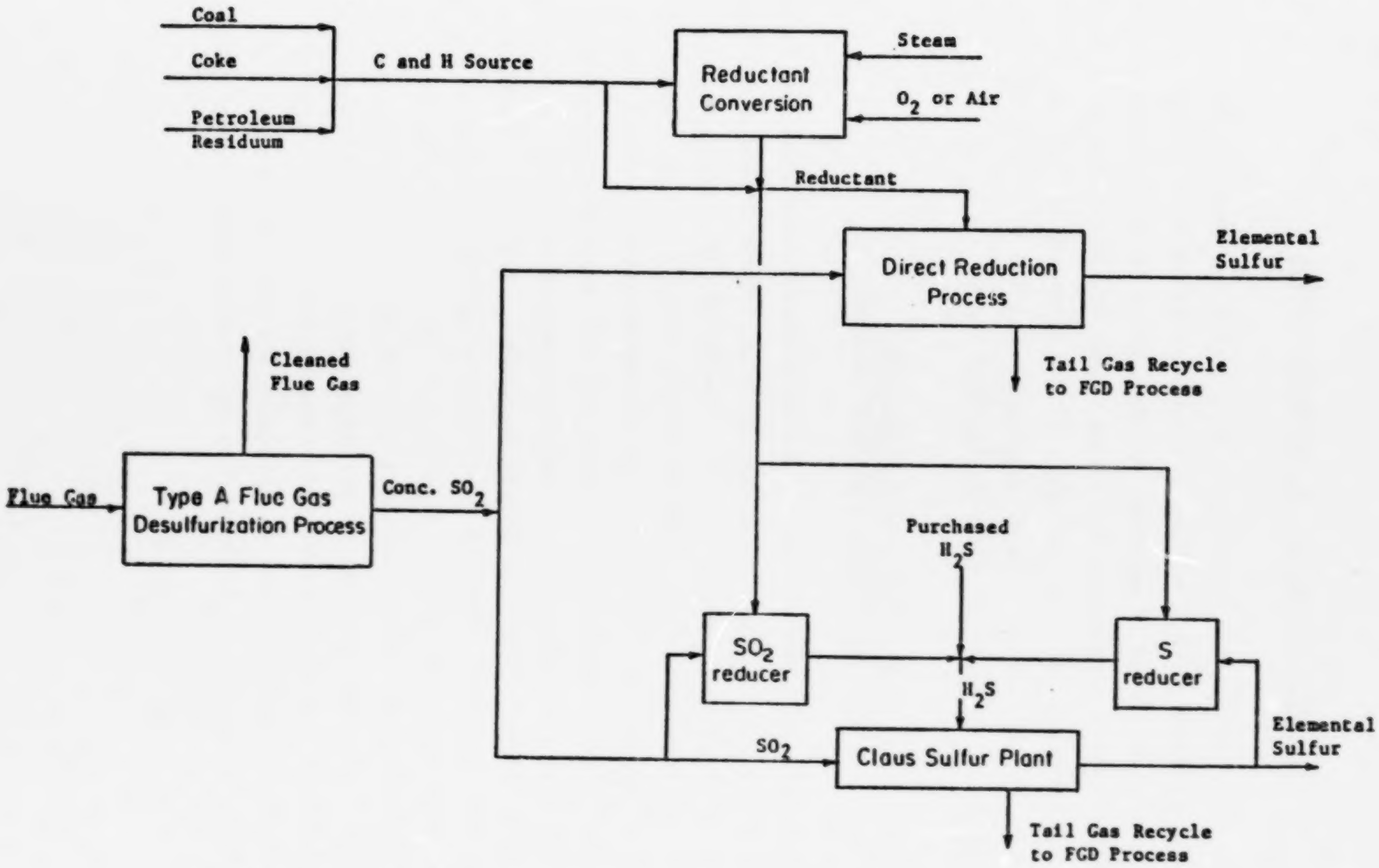

Coal
Coke
Petroleum Residuum
C and H Source
Reductant Conversion
Steam
O_2 or Air
Reductant
Direct Reduction Process
Elemental Sulfur
Tail Gas Recycle to FGD Process
Cleaned Flue Gas
Flue Gas
Type A Flue Gas Desulfurization Process
Conc. SO_2
Purchased H_2S
SO_2 reducer
S reducer
H_2S
SO_2
Claus Sulfur Plant
Elemental Sulfur
Tail Gas Recycle to FGD Process

FIGURE 4-1. POSSIBLE ROUTES TO ELEMENTAL SULFUR WITH TYPE A FLUE GAS DESULFURIZATION PROCESS

Within the scope of this study, the ultimate source of the reductant is coal, coke, or petroleum residuum. The ultimate reductant either can be used directly or can be converted into a more "convenient" (reactive) form. The reductant conversion step normally would be some type of gasification process which would convert the carbon and hydrogen in the original reductant into primarily H_2 and CO.

4.2 Type B FGD Processes (Those Requiring H_2S)

The possible routes to elemental sulfur which are within the scope of this study and apply to Type B flue gas desulfurization processes are shown in Figure 4-2. The H_2S required by this type of flue gas desulfurization process either can be purchased externally or can be generated by reducing part of the elemental sulfur product. For the latter route, the ultimate reductant again can be used directly or converted into another form.

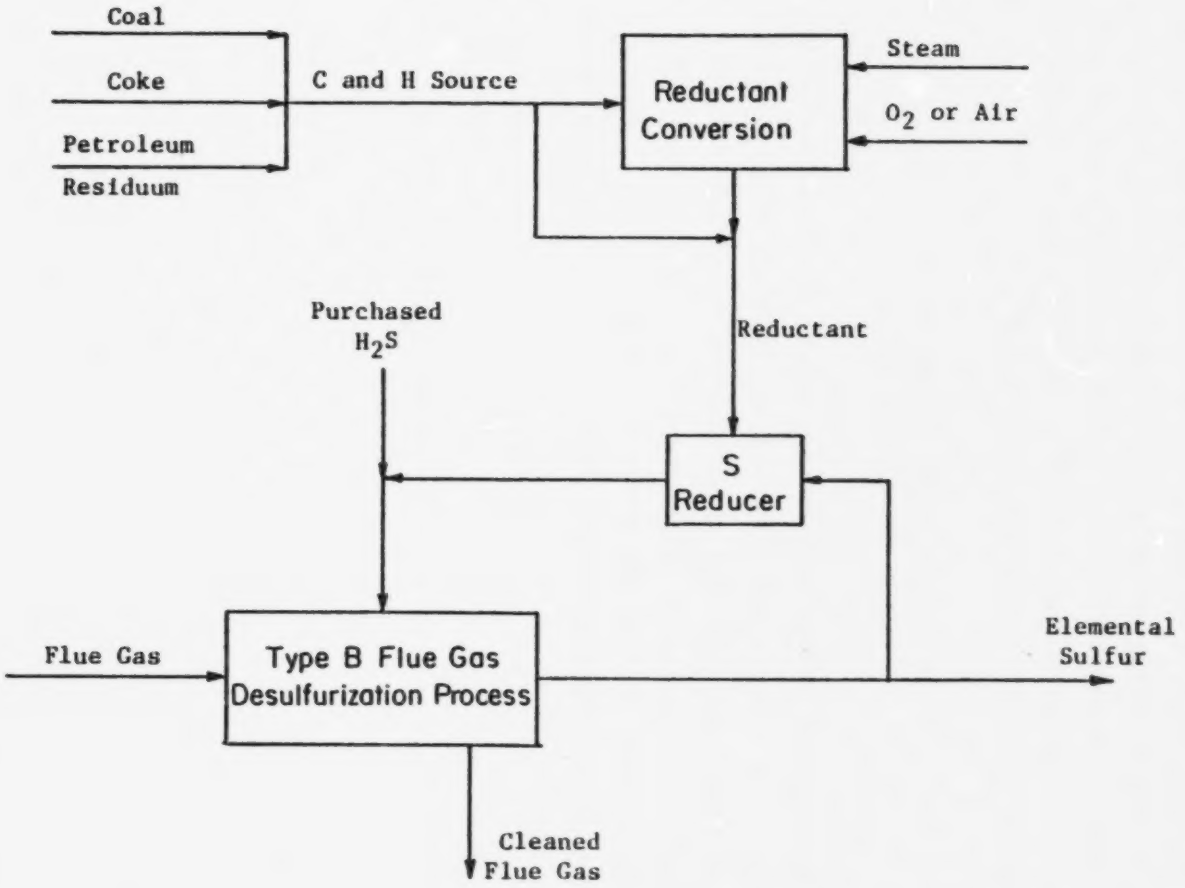

Coal
Coke
Petroleum
Residuum
C and H Source
Reductant Conversion
Steam
O_2 or Air
Reductant
S Reducer
Purchased H_2S
Flue Gas
Type B Flue Gas Desulfurization Process
Elemental Sulfur
Cleaned Flue Gas

FIGURE 4-2. POSSIBLE ROUTES TO ELEMENTAL SULFUR WITH TYPE B FLUE GAS DESULFURIZATION PROCESS

5. REDUCTANTS AND REDUCTION REACTIONS

In this section the state of the art of the technology for a number of reduction reactions is reviewed. These reactions and the types of flue gas desulfurization processes for which they are of interest are as follows:

Reduction	Types of FGD Process
SO_2 to S	Type A with direct reduction
SO_2 to H_2S	Type A with indirect reduction of SO_2 Type B with H_2S made from SO_2
S to H_2S	Type A with indirect reduction of S Type B with H_2S made from S

For each of these types of reductions a number of possible reductants will be discussed.

5.1 Reduction of SO_2 to Sulfur

Hydrogen as Reductant

Catalytic reduction of SO_2 by hydrogen has been studied by many investigators.(1,2) Recently, a kinetic model was proposed by a research group at the University of Akron,(2) using an activated bauxite as the catalyst. Sulfur dioxide is reduced according to the following chemical reaction:

$$SO_2 + 2H_2 \rightarrow 2H_2O + 1/2\ S.$$

However, an undesired side reaction is always occurring:

$$H_2 + 1/2\ S_2 \rightarrow H_2S.$$

That is, the reaction does not stop at elemental sulfur but goes on to form H_2S. Thus, SO_2 is reduced only partially to condensable elemental sulfur, and the remaining effluent gas is a mixture of H_2S and unreacted SO_2. Presumably, the mixed SO_2 and H_2S could be reacted in a separate Claus reactor to complete the conversion. However, the experimental results(2) indicate that total SO_2 conversion is low and consequently the H_2S/SO_2 ratio in the effluent is always far below 2.0, the ratio required for the Claus reaction. This is shown in the data presented in Table 5-1. Thus, it appears that the concept of reducing SO_2 with hydrogen but stopping at elemental sulfur has not been adequately demonstrated as of this time.

Carbon Monoxide as Reductant

In the presence of suitable catalysts, carbon monoxide has proven to be effective for reducing SO_2. The chemical reaction is

$$2CO + SO_2 \rightarrow 1/2\ S_2 + 2CO_2.$$

However, a parallel reaction produces noxious carbonyl sulfide (COS) at the expense of sulfur yield.

$$CO + 1/2\ S_2 \rightarrow COS.$$

Exploratory studies have been done by Chevron,(3) U.S. Bureau of Mines,(4,5) and the University of Massachusetts.(6-8) All of these were aimed at the removal of SO_2 from stack gas (typically 2000 ppm), with elemental sulfur as the end product. Copper on alumina has been found to be a preferred catalyst. Typical reaction time is about 0.2 seconds at temperatures above 425 C (800 F). The results of Quinlan, et al(7) indicate that SO_2 conversion increases with increasing temperature and CO/SO_2 feed ratio. Unfortunately, the undesired COS formation behaves in the same manner. These data are shown in Figure 5-1. Note that the formation of COS increases very rapidly as high SO_2 conversions are approached. The total SO_2 plus COS in the effluent gas goes through a minimum at about 90 percent SO_2 conversion, and at this point the COS concentration is about 1.5 times the SO_2 concentration.

When the reducing gas contains water vapor as well as CO, the COS formed can be hydrolyzed to H_2S. That is,

$$COS + H_2O \rightarrow H_2S + CO_2.$$

This reaction may require a catalyst different from that used for the reduction reaction. The product of a reduction plus hydrolysis scheme would be H_2S and not the desired elemental sulfur. Thus, it appears that the concept of reducing with CO to obtain elemental sulfur has not been adequately demonstrated as of this time.

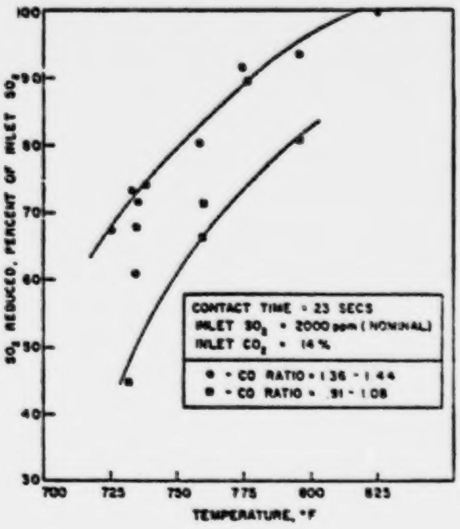
TABLE 5-1. DATA ON REDUCTION OF SO_2 WITH HYDROGEN

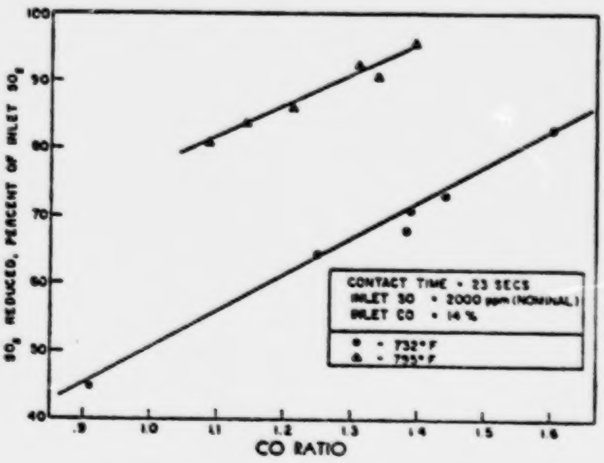
Initial Concentrations: SO_2 = 2.67 mole percent

H_2 = 5.33 mole percent

Temperature		Equilibrium Values		Experimental Data			
°C	°F	SO_2 Conversion (%)	S/H_2S Ratio	Residence Time (sec.)	SO_2 Conversion (%)	S/H_2S Ratio	H_2S/SO_2 Ratio
345	653	93.9	6.9	0.83	16.9	22.4	0.009
360	680	92.9	5.7	0.81	24.3	15.9	0.019
375	707	90.7	4.0	0.79	28.1	10.0	0.036
				1.59	44.9	7.5	0.096
390	734	89.6	3.4	0.78	36.8	7.7	0.067

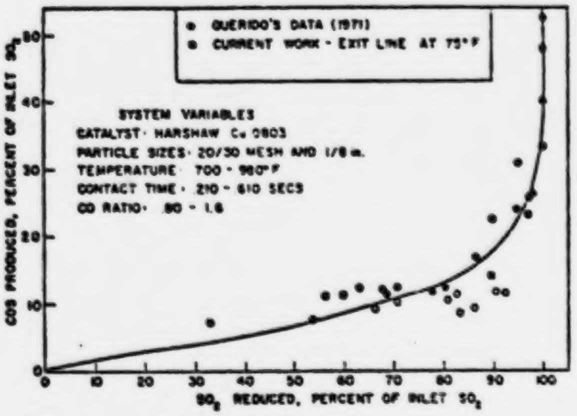
Source: Murdock, D. L. and Atwood, G. A., "Kinetics of Catalytic Reduction of Sulfur Dioxide with Hydrogen", Ind. Eng. Chem. Process Des. Develop. 13, No. 3, p. 254, 1974.



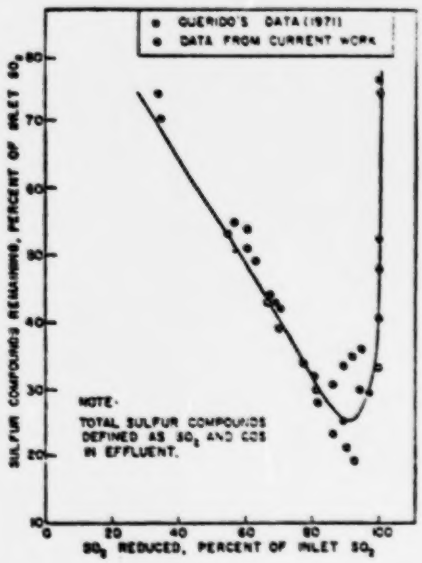


Dependence of SO_2 conversion on carbon monoxide concentration

Dependence of SO_2 conversion on temperature



Dependence of COS production on SO_2 conversion



Dependence on total remaining effluent SO_2 and COS upon SO_2 conversion

$$\text{CO Ratio} = \frac{\text{CO conc, ppm}}{(2)(SO_2 \text{ conc, ppm})}$$

Source: Quinlan, C. W., et al, "Kinetics and Yields for Sulfur Dioxide Reduction by Carbon Monoxide", Ind. Eng. Chem. Process Des. Develop., 12 (1), p 107, 1973.

FIGURE 5-1. DATA ON REDUCTION OF SO_2 WITH CARBON MONOXIDE

Hydrogen/Carbon Monoxide Mixtures as Reductant

The SO_2 reduction process which is being developed by the American Smelting and Refining Company (ASARCO) and Phelps Dodge Corporation(9,10) involves the reduction of SO_2 to sulfur using H_2/CO mixtures as the reductant. A pilot plant of this process is in operation at ASARCO's El Paso, Texas, copper-lead smelter. A flowsheet of this pilot plant is shown in Figure 5-2. Actually, ASARCO has developed the SO_2 reduction process and Phelps Dodge has developed the process for reforming natural gas to provide the reducing gas.

The ASARCO process uses a two-stage reactor system. In the first stage, the SO_2-rich stream and the H_2/CO-rich stream are reacted over a proprietary catalyst. The conversion of SO_2 to sulfur in this reactor is about 69 percent when reducing an SO_2 stream containing 12 percent SO_2 and is about 80 percent when reducing a pure SO_2 stream.(9) The gases are introduced into this reactor at a temperature of about 340 C (650 F). The reactor is a vertical shell-and-tube heat exchanger with catalyst in the tubes and a heat transfer fluid circulating through the shell side to control the reactor temperature.

The second stage is a Claus reactor. Part of the SO_2 is reduced to H_2S in the first stage, and the reaction conditions are adjusted to obtain the desired 2:1 H_2S/SO_2 ratio in the product gas.

The H_2/CO mixture used as the reductant in this process is generated by the partial oxidation of natural gas. The principal reaction is

$$CH_4 + 1/2\ O_2 \rightarrow 2\ H_2 + CO.$$

Thus, the reducing gas contains H_2 and CO in a molar ratio of 2:1. The overall SO_2 reduction reaction (both stages), therefore, can be written as

$$3/2\ SO_2 + 2\ H_2 + CO \rightarrow 3/4\ S_2 + CO_2 + 2\ H_2O.$$

The ASARCO reduction technology is very close to that required when a coal-based reducing gas is used (as will be seen later in the report), but one difference is that in the coal gas the H_2/CO ratio is not 2 but rather

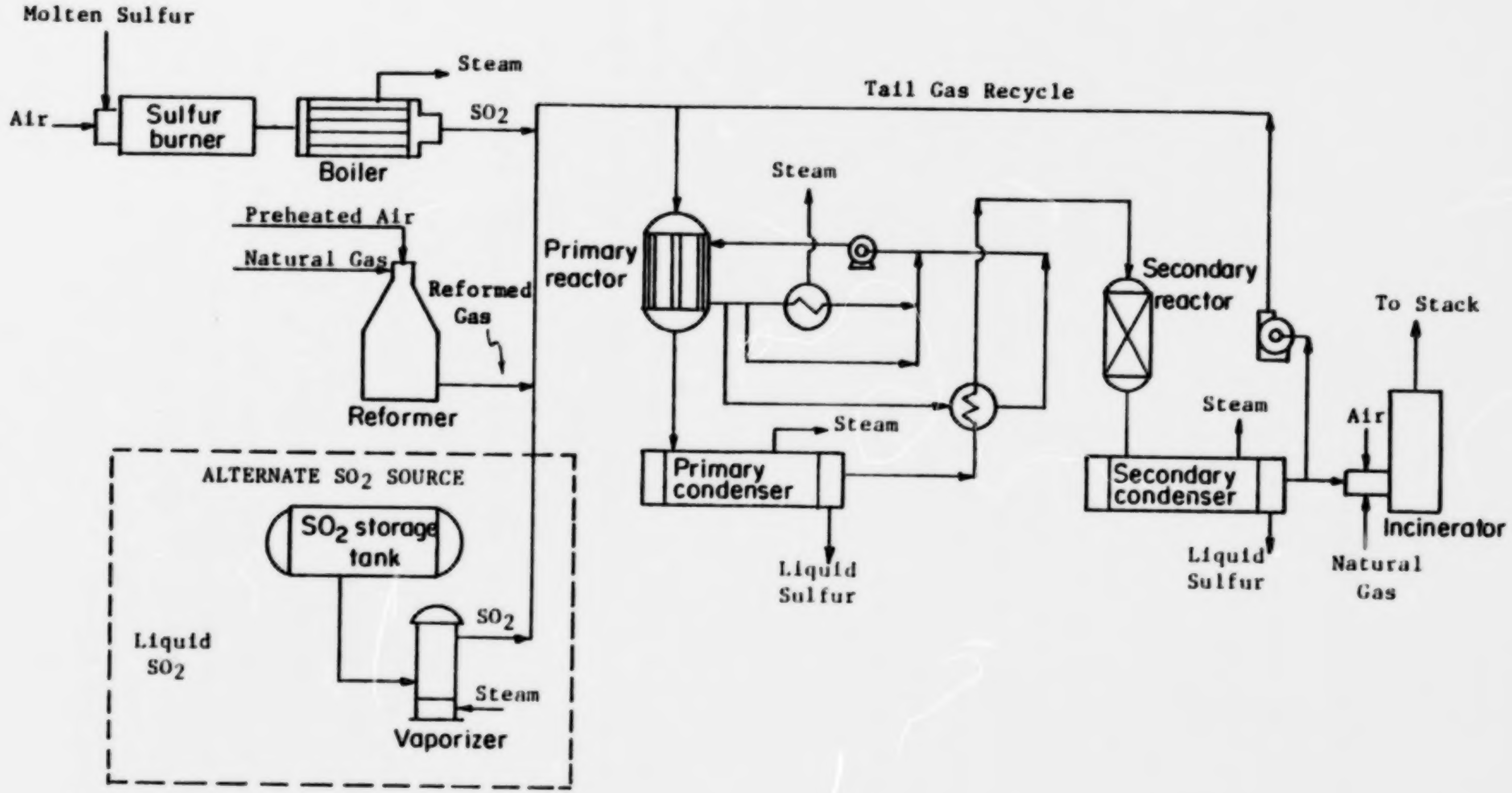

Molten Sulfur
Air
Sulfur burner
Boiler
Steam
SO_2
Tail Gas Recycle
Preheated Air
Natural Gas
Reformed Gas
Reformer
Primary reactor
Steam
Steam
Primary condenser
Liquid Sulfur
Secondary reactor
Steam
Secondary condenser
Liquid Sulfur
To Stack
Air
Incinerator
Natural Gas
ALTERNATE SO_2 SOURCE
SO_2 storage tank
Liquid SO_2
SO_2
Steam
Vaporizer

FIGURE 5-2. FLOWSHEET OF ASARCO-PHELPS DODGE SO_2 REDUCTION PILOT PLANT

about 0.5-0.6. The water gas shift reaction

$$CO + H_2O \rightarrow H_2 + CO_2$$

can be used to increase the H_2/CO ratio, but this adds another step to the process. An important question is whether a gas with an H_2/CO ratio as low as 0.5 can be used in the ASARCO reduction system. ASARCO is now studying the use of coal gas as a reductant in their system.

If the H_2/CO molar ratio in the reducing gas is designated as R, then the general overall equation for the desired SO_2 reduction is

$$SO_2 + \frac{2R}{R+1} H_2 + \frac{2}{R+1} CO \rightarrow 1/2\ S_2 + \frac{2}{R+1} CO_2 + \frac{2R}{R+1} H_2O.$$

Two moles of H_2 + CO are required per mole of SO_2.

Natural Gas as Reductant

The SO_2 reduction process which has been developed by the Allied Chemical Company$^{(10-12)}$ accomplishes a reduction of SO_2 to sulfur using natural gas as the reductant. A flowsheet of this process is shown in Figure 5-3. The process is similar to the ASARCO process except that the natural gas is used directly instead of being reformed. The process uses a two-stage reactor system. In the first stage, the SO_2-rich stream and natural gas are fed to a reactor containing a special, proprietary catalyst. About 40 percent of the inlet SO_2 is converted to sulfur in this reactor, and this fact makes this process appropriate for discussion in this section. The overall reaction involved is:

$$CH_4 + 2\ SO_2 \rightarrow S_2 + CO_2 + 2\ H_2O.$$

H_2S is clearly an intermediate in this reaction; Allied states that one of the accomplishments in the primary reduction stage is to generate sufficient H_2S to provide a 2:1 H_2S/SO_2 ratio for the ensuing Claus reaction. The important fact is that Allied's catalyst does result in some reduction of SO_2 to sulfur in a single step.

Since only about 40 percent of the SO_2 is reduced to sulfur directly in the first stage, a Claus reactor is used as a second stage to recover the rest of the sulfur. Some SO_2 is reduced to H_2S in the first

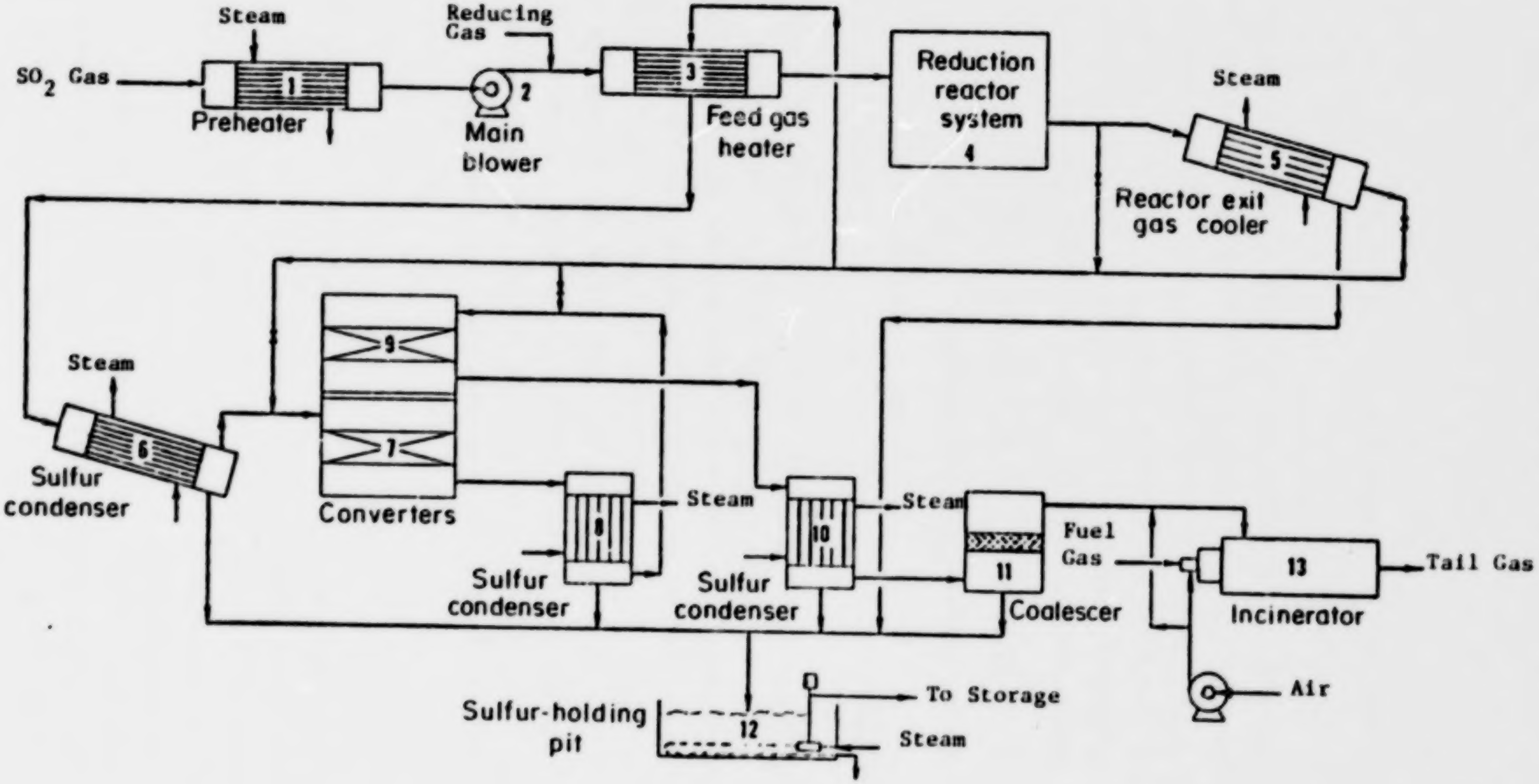

SO_2 Gas
Steam
1
Preheater
Reducing Gas
2
Main blower
3
Feed gas heater
Reduction reactor system 4
Steam
5
Reactor exit gas cooler
Steam
6
Sulfur condenser
9
7
Converters
8
Steam
Sulfur condenser
10
Steam
Sulfur condenser
11
Coalescer
Fuel Gas
13
Incinerator
Tail Gas
Air
Sulfur-holding pit
12
To Storage
Steam

FIGURE 5-3. ALLIED CHEMICAL SO_2 REDUCTION PROCESS

stage, and the reaction conditions are adjusted to get the desired 2:1 H_2S/SO_2 ratio in the product gases. The Allied process reportedly produces very little COS and CS_2.

The feasibility of this process has been demonstrated commercially by treatment of the SO_2 effluent stream from smelters at the Falconbridge Nickel Mines, Ltd. facility near Sudbury, Ontario, Canada. Since this process requires natural gas, it is not considered "acceptable" within the scope of this study but rather is used as a baseline for comparison with other options. It should be noted that Allied is now working on the extension of this process to higher molecular weight hydrocarbon feedstocks.

Hydrogen Sulfide as Reductant

The reduction of SO_2 with H_2S is the basis of the commercially proven Claus process. This process is shown as part of the Allied process in Figure 5-3. In this figure, converters 7 and 9 and the following equipment constitute the Claus plant. A two-stage catalytic converter with intercooling and condensing is used. A bauxite catalyst is used. The reaction temperatures are 230-400 C (450-750 F), with lower temperatures maintained in the second stage than in the first stage.(13) This is done because the reaction is exothermic and the equilibria are less favorable at higher temperatures. The conversion is 70-80 percent in the first stage and about 95 percent overall. A third stage can be used to increase the conversion somewhat, but this is not justified when the Claus plant follows an SO_2 recovery facility to which the tail gas can be recycled. The tail gas must be oxidized before being recycled in order to convert the H_2S into SO_2.

Coal as Reductant

The RESOX process(14,15) developed by Foster-Wheeler Corporation employs anthracite as a noncaking, low-volatile, solid carbon reducing agent for SO_2, with elemental sulfur as the end product. The overall reaction is

$$C + SO_2 \rightarrow CO_2 + 1/2\ S_2.$$

In the RESOX process, rice-size anthracite enters the top of a vertical tubular reactor by gravity through a rotary airlock valve. The concentrated

SO_2 stream flows countercurrently upward with air injected at several ports around the lower vessel circumference. The reactor is operated under atmospheric pressure in the temperature range of 590-820 C (1100-1500 F). Typical gas residence time is 3-4 seconds. Foster-Wheeler reports that conversion of 90-95 percent of the inlet SO_2 to elemental sulfur can be realized.

This process was scheduled for commercial demonstration at Gulf Power Company's Scholz Plant at Chattahoochee, Florida, during 1975. However, these tests, at least on the reduction process, have not been successful as of this writing.

5.2 Reduction of SO_2 to H_2S

Hydrogen/Carbon Monoxide Mixtures as Reductant

SO_2 can be reduced all the way to H_2S with hydrogen and/or carbon monoxide. A high activity hydrogenation catalyst can be used for this purpose, and the cobalt-molybdenum catalysts used extensively for hydrogenation reactions would appear to be a logical choice. However, the use of such a catalyst for reducing a concentrated (>25%) SO_2 stream has not yet been demonstrated. Reduction of dilute (<5%) SO_2 streams has been done as part of two Claus tail gas treatment processes, and reduction of a concentrated stream has been proposed by Shell as part of their FGD process. These items will be discussed in this section.

The ability of CO to serve as a reducing agent arises through intermediate reactions involving water vapor, such as

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad \text{(water-gas shift)}$$

$$COS + H_2O \rightarrow H_2S + CO_2 \qquad \text{(COS hydrolysis).}$$

The water vapor can be either initially present in the gas or generated by the reactions involving hydrogen. If the H_2/CO molar ratio in the reducing gas is designated as R, then the general overall equation for the reduction reaction is

$$SO_2 + \frac{3R}{R+1} H_2 + \frac{3}{R+1} CO \rightarrow H_2S + \frac{3}{R+1} CO_2 + \frac{2R-1}{R+1} H_2O.$$

The two Claus tail gas treatment processes in which H_2/CO mixtures are used to reduce SO_2 are the Shell Claus Offgas Treating (SCOT) process(10,16) and the Beavon sulfur removal process.(10,17) In both processes the reduction step converts all the sulfur compounds in the tail gas to H_2S, which is then recovered. The H_2S recovery is done by amine scrubbing in the SCOT process and by the Stretford system for the Beavon process.

In the SCOT process the reduction is conducted over a bed of cobalt-molybdenum on alumina catalyst at a temperature of about 300 C (570 F). With an excess of reductant, virtually complete conversion to H_2S is obtained. The water-gas shift reaction is very rapid at the conditions of the SCOT process. The presence of CO in the reducing gas results in an increased reaction rate as compared with reduction with H_2 alone. This is shown in Figure 5-4. At the SCOT conditions the concentrations of COS and CS_2 in the effluent gas from the reducer approach the thermodynamic equilibrium values. Methanation reactions are negligible.

The Beavon process also uses a cobalt-molybdate catalyst and uses "moderate conditions of temperature and pressure, resembling those in the Claus unit."(17) The catalyst is "very effective in reacting water vapor present with carbon monoxide to form hydrogen, or reacting the water vapor with COS and CS_2 to give H_2S."(17) The space velocity of tail gas plus reductant in the reduction reactor is about 2000 vol/hr/vol of catalyst.(10) The catalyst is reasonably rugged but evidently can be damaged by some trace species. Reference 17 states "Because there are no heavy metals or halogens to poison the catalyst, or tars to clog the system, the catalyst should last for several years."

It should be re-emphasized that, as tail gas treatment processes, the SCOT and Beavon processes are designed for SO_2 streams containing less than 5 percent SO_2.

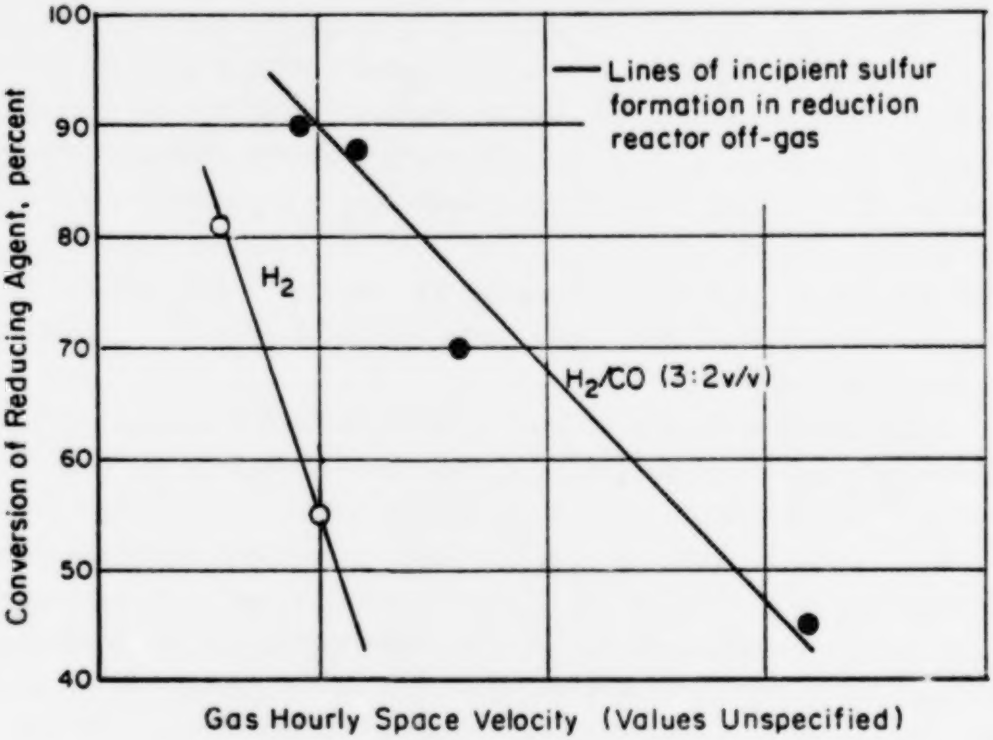
The SO_2 reduction system proposed by Shell for use with their FGD process is shown in Figure 5-5.(18) The reduction occurs in three stages with intercooling, the last two stages being Claus reactors. The first stage, labeled "partial reduction reactor", involves a reduction of SO_2 to H_2S with a H_2/CO mixture. Neither the intended catalyst nor the H_2/CO ratio are specified. This reduction system has been proposed by Shell but has not been demonstrated in conjunction with the basic Shell FGD process.

Test Conditions

Catalyst : Co/Mo On Alumina

Temperature : About 300 °C

Gas Composition (% Vol) : SO_2 0.8; H_2S 1.5; S(AS S_1) 0.4; CO_2 30; H_2O 25; H_2(+CO) 3 - 11; N_2 Balance



Source: Reference 16.

FIGURE 5-4. REDUCTION OF SULFUR COMPOUNDS AS FIRST STEP IN SHELL CLAUS OFFGAS TREATING (SCOT) PROCESS

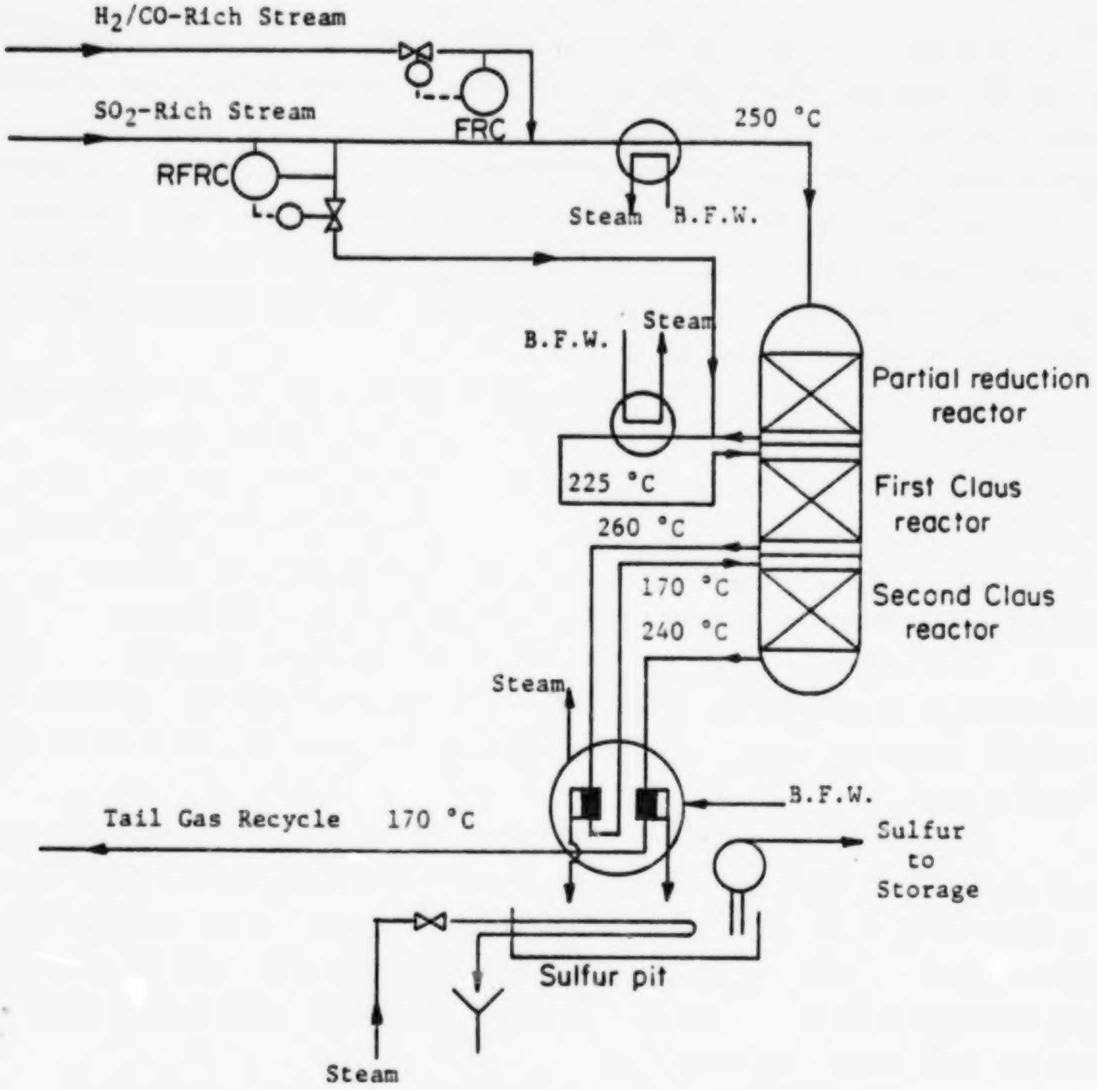

H$_2$/CO-Rich Stream
SO$_2$-Rich Stream
FRC
RFRC
250 °C
Steam
B.F.W.
B.F.W.
Steam
Partial reduction reactor
225 °C
First Claus reactor
260 °C
170 °C
Second Claus reactor
240 °C
Steam
B.F.W.
Tail Gas Recycle
170 °C
Sulfur to Storage
Sulfur pit
Steam

FIGURE 5-5. FLOWSHEET OF CONCEPTUAL REDUCTION SYSTEM PROPOSED FOR SHELL FGD PROCESS

6. USE OF PURCHASED HYDROGEN SULFIDE

The possibility of using purchased hydrogen sulfide as a reductant for flue gas desulfurization processes has been mentioned in previous sections. An analysis was made of the feasibility of this option. This analysis is summarized in this section, and additional details are presented in Appendix B.

Problems associated with the use of hydrogen sulfide as a reductant include: extreme toxicity, corrosion properties, explosive hazard, transportation, storage, adequate supply and unfamiliarity with the product by operating personnel at electricity generating plants.

It is estimated that for 1974, the total hydrogen sulfide potentially available from refineries and natural gas plants in the United States was approximately 15.2×10^3 metric tons per day, increasing to approximately 21.4×10^3 metric tons per day by 1980. This is the total hydrogen sulfide from all sources and includes the large percentage converted to elemental sulfur in Claus plants or burned to SO_2 and vented to the atmosphere.

It is expected that plants in which coal or oil is gasified or desulfurized will provide additional potential sources of hydrogen sulfide in the future; however, their contribution to national production will be insignificant through 1985.

Sulfur dioxide emissions from fossil-fired plants will exceed the potential supply of hydrogen sulfide for use as a reductant in all power plants by a factor of at least 3 in 1980. The potential demand for hydrogen sulfide is much greater than any anticipated supply. Nevertheless, there is potentially enough hydrogen sulfide available to reduce a significant fraction of the sulfur oxides produced at power plants.

Hydrogen sulfide presently is available at prices ranging from \$143 to \$221 per metric ton (6.5-10 cents per pound),* f.o.b., and most hydrogen sulfide probably is sold at the lower figure. The current prices have little relevance to the price of large volumes of hydrogen sulfide that might be required by an electric utility as a reductant (approximately

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* Because of the dominance of English units of measurement in the industries to which this report is addressed, some English units are used in this report. Both units are often given together. A table of conversion factors between English and metric units is presented in Appendix H.

693,000 liters [183,000 gallons] per day for a 1000-MW power plant), and the price would probably be equal to or slightly less than the price of the contained sulfur. Results contained in Section 11 of this report indicate that the cost of producing H_2S via gasification of coal or residual oil would be between \$55 and \$71 per metric ton (2.5-3.2 cents per pound) of H_2S, depending on the feedstock cost and plant size. Thus, a power plant having access to an "across the fence" source of H_2S would probably need to purchase H_2S at these price levels or lower for this approach to prove economically attractive. Another factor to consider is that if H_2S is purchased by an electric utility to reduce the SO_2 it generates, the utility is tripling the amount of sulfur that it has to market.

At the present time, liquefied hydrogen sulfide is transported only by truck or railroad car at a cost of approximately 3 to 4 cents per metric ton-mile. Barge transportation probably would cost less but would be of limited applicability. Pipeline transportation is impractical except for short distances. It may be feasible if the power plant is located in the vicinity of a refinery or other hydrogen sulfide source.

In summary, the potential supply of hydrogen sulfide is sufficient to handle only a portion of the power plants which will be installing FGD systems. Geographical considerations will further restrict the use of hydrogen sulfide at power plants. Thus, it is concluded that purchased hydrogen sulfide will play only a minor role as a reductant for FGD systems.

7. GENERATION OF REDUCING GAS BY GASIFICATION

Before quantifying the trace constituents in gasifier-produced reductant gases and defining their effects on FGD systems, it is necessary to examine the characteristics of the gasification systems themselves. Coal and petroleum residuum can be gasified with steam and oxygen (or air) to produce a gas rich in hydrogen and carbon monoxide. This gas can be used as a fuel, either directly or after upgrading to increase its heating value. However, the intention in this study is to use this gas not for its fuel value but for its reducing power.

The consideration in this study is limited to gasification systems which are commercially proven and available. For the gasification of coal, the consideration is also limited to gasifiers operating near atmospheric pressure. This is so because the reducing gas is required only at low pressure, since the FGD processes with which it will be used operate at essentially atmospheric pressure. Thus, there is no reason to incur the additional complication and expense of a lock-hoppering system for feeding the coal into a pressurized gasifier. The following atmospheric pressure gasifiers are accepted as commercially proven and available for commercial usage in the U.S.:

(1) Koppers-Totzek gasifier
(2) Wellman-Galusha gasifier
(3) Winkler gasifier
(4) Riley-Morgan gasifier.

For the gasification of petroleum residuum, the following gasification processes are commercially available:

(1) Shell Gasification Process
(2) Texaco Synthesis Gas Generation Process.

These processes operate on a variety of petroleum feedstocks including atmospheric and vacuum residua. Also, coal tar can be used as a feedstock for the Texaco process.

Additional information on the gasification processes listed above is presented in Appendix C. The following sections highlight the features of these processes and the compositions of the gases that they produce.

7.1 Coal Gasification Processes

The Koppers-Totzek gasifier must be blown with oxygen (or at least an oxygen/air mixture) to reach the high operating temperature used. The other three gasifiers can be blown with either oxygen or air. When oxygen is used, these gasifiers generate a gas which contains primarily H_2 and CO and only very little N_2 (usually 1-2 percent). When air is used, the gas is diluted by the N_2 in the feed air, the N_2 concentration being about 50 percent. As compared with air-blown systems, the oxygen-blown systems will result in:

- Smaller gasification vessels, gas cleanup systems, reduction reactors, and gas transfer ducts
- Higher reaction rates in the reduction reactors because of higher partial pressures of the reacting species.

The decreased investment for the smaller equipment tends to be offset by the cost of the oxygen plant. Differences in operating cost items are also important, such as the fact that oxygen plants require considerable quantities of electrical power. The choice between air- and oxygen-blown systems requires a detailed analysis of the entire gas generation and utilization system for the specific situation involved.

For a 1000-MW power plant fired with 3.5 percent sulfur coal, the gasification system to supply reductant for the FGD process will be equivalent to about 270 metric tons/day of coal feed and to about 1.4×10^9 kcal/day (5.6×10^9 Btu/day) of gas output. This corresponds to several of the smaller gasifiers or one of the larger ones (Koppers-Totzek two-headed). For comparison, the feed rate of coal to the power plant itself is about 8,840 metric tons/day. If the gasifiers are oxygen-blown, the capacity of the oxygen plant will be about 200 metric tons O_2/day.

The operating characteristics of the four coal gasifiers are compared in Table 7-1. Due to very high temperature operation, the K-T does not produce ammonia or methane in any significant quantities, but the gas contains up to 50 percent of the ash in the coal as fly ash. The K-T has the lowest overall thermal efficiency (67 percent) of the four gasifiers, whereas the Wellman-Galusha has the highest efficiency (82 percent).

TABLE 7-1. COMPARISON OF SELECTED COMMERCIAL ATMOSPHERIC PRESSURE COAL GASIFIERS

Oxidizing medium	Oxygen-Steam				Air-Steam		
Gasifier	Koppers-Totzek	Riley-Morgan	Wellman-Galusha	Winkler	Riley-Morgan	Wellman-Galusha	Winkler
Supplier	Koppers Company Inc., Pittsburgh, Pa.	Riley-Stoker Corp., Worcester, Mass.	McDowell-Wellman Engg. Co., Cleveland, Ohio	Davy Powergas, Lakeland, Fla.			
Gasifier Bed Type	Entrained	Fixed-bed	Fixed-bed	Fluidized	Fixed-bed	Fixed-bed	Fluidized
Commercial Units Built	53	1	0	20	0	3	16
Gas Discharge Conditions							
Temperature, C (F)[(a)]	1490 (2700)	650 (1200)	680 (1250)	980 (1800)			
Pressure, inches water (gauge)	70	35	70	30	35	70	30
Composition, mole percent							
CO	56	41	52	40	26	29	34
H_2	35	39	33	37	19	15	31
CO_2	7	16	12	18	4	3.4	12
CH_4	0	3	1	3	1.6	2.7	0.5
CH_4^+	0	0.7	0	--	0.2	0	--
N_2 + Ar	2	0.5	2	2	50	50.3	22.5
H_2S, etc.	(b)	(b)	(b)	(b)	(b)	(b)	(b)
HHV, Btu/scf	290	305	282	280	163	170	120
Gas Produced, scf/lb coal (approx.)	31	33	ND	26	ND	65-68	ND
Overall Thermal Efficiency, percent	67	70	82	76			
Turndown, percent of full load	35 (2-burner) 65 (4-burner)	ND	90	50-150			
Feed Coal Size	90%(-200)mesh	ND	1/2 - 2 inches	<3/8 in.			
Pure Oxygen Feed, lb/10^6 Btu cold gas	80		90	70	NA	NA	NA
Steam Feed, lb/10^6 Btu cold gas	30	86	50	20			
Export Steam Produced, lb/10^6 Btu cold gas	173	0	62	ND	ND	ND	ND
Coal feed, lb/10^6 Btu cold gas	114	110	94	140			
Oxygen/Coal Weight Ratio	0.7	0.46	ND	0.5	NA	NA	NA
Gasification Rate, lb coal/hr-ft^3	16[(c)]	ND	99/ft^2	2-4	ND	ND	ND

(a) Before waste heat boilers at gasifier exit.

(b) Depends on coal sulfur content. Usually about 0.6 percent for 2 percent sulfur coal, oxygen-blown gasifier.

(c) For 2-burner gasifier; 28 for 4-burner gasifier.

NA = Not applicable; ND = No data.

Conversion factors: kg/m^2 = 25.40 (inches water), kcal/std m^3 = 8,935 (Btu/scf), std m^3/kg coal = 0.06243 (scf/lb coal), kg/10^6 kcal = 1.793 (lb/10^6 Btu).

All the gasifiers generate CO and H_2 with the ratio CO/H_2 greater than 1. For some applications, a lower CO/H_2 ratio (i.e., more H_2) may be desired. This ratio can be affected, but only slightly so, by changing the ratios of steam and O_2 (or air) to coal fed to the gasifier. Shifting the CO to make more H_2 is also possible, since sulfur-resistant shift catalysts are available.

7.2 Residual Oil Gasification Processes

Typical gas compositions for the two heavy oil gasification processes are given in Table 7-2.

TABLE 7-2. TYPICAL GAS COMPOSITIONS FROM OIL GASIFICATION PROCESSES

(Dry Basis)

	Shell Process				Texaco Process
Feedstock	Heavy Fuel Oil	Propane Asphalt	Vacuum Residuum		Straight Residuum
Oxidizing Medium	Oxygen	Oxygen	Oxygen	Air	Oxygen
Composition, volume percent					
H_2	46.7	44.2	47.1	14.5	47.0
CO	46.2	47.8	50.8	23.6	47.0
CO_2	4.3	4.5	1.2	1.0	5.6
CH_4	0.6	0.6	0.6	0.2	0.1
N_2 + argon	1.4	1.3	1.2	60.7	0.2
H_2S and COS[(a)]	0.8	1.6	0.04	0.02	0.1

(a) Depends on feed sulfur content.

8. TRACE CONSTITUENTS IN GASIFIER PRODUCTS

Available experimental data on trace constituents in products from various gasifiers are presented in this section. These data are scanty and do not provide a sufficient basis for evaluating the effects of trace substances on user processes. Therefore, thermodynamically calculated values of the equilibrium composition in gases at various temperatures are presented based on a modified equilibrium constant approach. Because of the need to compare the relative contribution of trace constituents by both the flue gas being scrubbed and the coal gas used for sulfur production, the trace constituent analyses of coal-fired boiler flue gas also are presented.

8.1 Experimental Data on Gasifier Product Trace Constituents

Koppers-Totzek Gasifier

Experimental trace constituent data on the K-T gasifier are limited to the concentrations of gaseous species in product gases.(19,20,21) All operating K-T gasifiers are located outside the USA in countries where public concern for the environment is less intense than in this country. However, available trace data are tabulated (Table 8-1) as a function of coal sulfur content and heating value. It can be noted that the total sulfur compounds formed are about 0.3 mole percent when the feed coal has 1 percent sulfur. Acid gas treatment steps can be employed to reduce the sulfur content.

Wellman-Galusha Gasifier

Data on W-G gasifier trace constituents are not available. Thus, the computer calculated values will be the only source of data. Also, since the Riley-Morgan gasifier operating conditions are very similar

TABLE 8-1. EXPERIMENTAL DATA ON KOPPERS-TOTZEK GAS TRACE CONSTITUENTS

Reference Number	20	20	20	21	22	
Gas Location	Gasifier Outlet	To Compression and Acid Gas Removal	Product Gas	After Acid Gas Removal	Gasifier Outlet	
Coal						
Ash, weight percent				17.3	22.14	19.12
S, weight percent				0.95	0.67	4.88
HHV, Btu/lb				8,830	9,888	11,388
Gas Composition, (volume percent dry basis)						
CO	52.76	52.77	53.17	60.88	58.68	55.38
H_2	35.55	35.55	36.52	32.60	32.86	34.62
CO_2	10.07	10.04	9.44	5.23	7.04	7.04
N_2	0.42	0.43	0.44	1.16	1.12	1.01
CH_4	0.11	0.12	0.12	0.10	--	--
H_2S	0.32	0.32	3 vppm	0.02	0.28	1.83
COS	0.025	0.025	1.5 vppm	0.01	.02	0.12
SO_2	31 vppm	16 vppm	0.5 vppm			
NH_3	0.24	0.23	1 vppm			
HCN	0.041	0.032	1 vppm			
NO	10 vppm	7 vppm	3 vppm			
Ar	0.45	0.45	0.46			
Particulate matter, grains/scf	11.57 11.57	0.002 0.002	0.002 0.002			

Conversion factors: kcal/kg = 0.5578 (Btu/lb), grams/std m^3 = 2.288 (grains/scf).

to the W-G operating conditions, the experimental data presented for the R-M gasifier can be adapted if necessary to the W-G unit. Further, there are no operating oxygen-blown W-G gasifiers, so that obtaining experimental trace constituents data on W-G gasifiers will not be possible.

Riley-Morgan Gasifier

For an oxygen-blown R-M gasifier the available experimental trace constituent data for raw and clean gases are presented in Table 8-2. It can be seen that the data are totally inadequate with respect to trace elements. However, ammonia is present in the clean gas, even after liquid scrubbing, to the extent of 1800 ppm (0.18 volume percent). The effect of ammonia on the Claus catalyst should be watched.

Winkler Gasifier

Although commercial Winkler gasifiers have operated for over 30 years, the product gas has not been analyzed for trace constituents. A U.S. team which visited commercial gasification plants during 1974 has reported that the staff of Azot Sanayii (Kutahya, Turkey) was engaged in analyzing various streams for heavy metals.(21) This did not include the actual product gas analyses. Thus, experimental data on trace constituents are not available for the Winkler gasifier.

Synthane Process

During 1973-75, a series of gasification tests was run in the Synthane process development unit at Bruceton, Pennsylvania, to define the trace elements' distribution in gasifier effluents.(22) The gasifier operates at 40 atmospheres pressure and has a capacity of 20-40 lb/hr coal. Trace elements in the gas were determined by neutron activation "but results were incomplete and not conclusive" due to the extremely small amounts of trace metals present. For example, Hg, the only element measured, was on the order of 0.0001 ppm by weight.

TABLE 8-2. TRACE CONSTITUENT DATA FOR RILEY-MORGAN GASIFIER

(Oxygen-Blown System)

	Raw Gas	Clean Gas
Particulate matter, grains/scf	1.75	0
Tar, grains, scf	15.00	0.003 (submicron aerosol)
Ammonia, ppmv	2000	1800
HCN, ppmv	<100	traces
H_2S, ppmv	3000	1200[(a)]
COS, ppmv	300	250[(a)]
CS_2	traces	
Tar Level		
Btu/scf		300
Coal Data		
Ash, weight percent	8.0	
Sulfur, weight percent	1.0	
HHV, Btu/lb	14,000	

(a) These levels can be reduced to any desired lower value by further scrubbing.

Source: Extracted from letter correspondence between BCL and Riley Stoker Corporation, Worcester, Mass.

Conversion factors: grams/std m^3 = 2.288 (grains/scf), kcal/std m^3 = 8.935 (Btu/scf), kcal/kg = 0.5578 (Btu/lb).

Hygas Process

An experimental program has been conducted at the Institute of Gas Technology using samples from their pilot plant of the Hygas process. This process is fundamentally different from the other gasification processes discussed in this report in that it involves a hydrogasification of coal with a hydrogen-rich gas stream instead of using oxygen or air. This increases the production of methane in the gasifier. The hydrogasification is conducted at about 650 C (1200 F) and 74 atmospheres pressure.(23)

The first phase of this program(23) involved analyses of the coal and of solid materials at various stages of processing. No gas samples were analyzed. Assessment of these data indicate that significant fractions of the arsenic, cadmium, lead, mercury, selenium, and tellurium in the coal went into the gas. However, the report stated that "since these results are based on a limited number of samples, further analysis of a larger number of samples is required before any firm conclusions can be drawn".

The second phase of this program did involve some analyses of gas samples, but the results have not yet been published. Preliminary results(24) indicate the presence of some arsenic, selenium, and germanium in the gas.

The above discussions illustrate the extent of data unavailability as well as the difficulty involved in chemically analyzing the gas for trace constituents when they are present in parts per billion levels. A partial solution to circumvent these difficulties will be to estimate trace constituents in the gas by employing thermodynamic equilibrium calculations based on reactivity and volatility of the trace constituents. Data from this approach are presented as follows.

TABLE 8-3. MEAN ANALYTICAL VALUES FOR CONSTITUENTS IN 101 DIFFERENT COALS ON WHOLE-COAL BASIS

Constituent	Mean	Standard Deviation	Minimum	Maximum
As	14.02 ppm	17.70	0.50	93.00
B	102.21 ppm	54.65	5.00	224.00
Be	1.61 ppm	0.82	0.20	4.00
Br	15.42 ppm	5.92	4.00	52.00
Cd	2.52 ppm	7.60	0.10	65.00
Co	.57 ppm	7.26	1.00	43.00
Cr	13.75 ppm	7.26	4.00	54.00
Cu	15.16 ppm	8.12	5.00	61.00
F	60.94 ppm	20.99	25.00	143.00
Ga	3.12 ppm	1.06	1.10	7.50
Ge	6.59 ppm	6.71	1.00	43.00
Hg	0.20 ppm	0.20	0.02	1.60
Mn	49.40 ppm	40.15	6.00	181.00
Mo	7.54 ppm	5.96	1.00	30.00
Ni	21.07 ppm	12.35	3.00	80.00
P	71.10 ppm	72.81	5.00	400.00
Pb	34.78 ppm	43.69	4.00	218.00
Sb	1.26 ppm	1.32	0.20	8.90
Se	2.08 ppm	1.10	0.45	7.70
Sn	4.79 ppm	6.15	1.00	51.00
V	32.71 ppm	12.03	11.00	78.00
Zn	272.29 ppm	694.23	6.00	5,350.00
Zr	72.46 ppm	57.78	8.00	133.00
Al	1.29 %	0.45	0.43	3.04
Ca	0.77 %	0.55	0.05	2.67
Cl	0.14 %	0.14	0.01	0.54
Fe	1.92 %	0.79	0.34	4.32
K	0.16 %	0.06	0.02	0.43
Mg	0.05 %	0.04	0.01	0.25
Na	0.05 %	0.04	0.00	0.20
Si	2.49 %	0.80	0.58	6.09
Ti	0.07 %	0.02	0.02	0.15
Org. S[a]	1.41 %	0.65	0.31	3.09
Pyr. S	1.76 %	0.86	0.06	3.78
Sul. S	0.10 %	0.19	0.01	1.06
Tot. S	3.27 %	1.35	0.42	6.47
SXRF	2.91 %	1.24	0.54	5.40
Ash	11.44 %	2.89	2.20	25.80
Btu	12,748.91	464.50	11,562.00	14,362.00
C	70.28 %	3.87	55.23	80.14
H	4.95 %	0.31	4.03	5.79
N	1.30 %	0.22	0.78	1.84
O	8.68 %	2.44	4.15	16.03

(a) Abbreviations other than standard chemical symbols: organic sulfur (Org. S), pyritic sulfur (Pyr. S), sulfate sulfur (Sul. S), total sulfur (Tot. S), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (Mois.), volatile matter (Vol.), fixed carbon (Fix. C), high-temperature (HTA), low-temperature ash (LTA).

Source: Reference 25.

8.2 Thermodynamically Predicted Trace Constituent Data

Thermodynamic predictions were made of the distribution of species between the gaseous and condensed phases for a number of sets of operating conditions. These calculations were based on the average analysis for 101 coals determined by the Illinois Geological Survey,(25) which is shown in Table 8-3. The operating conditions for the gasifiers, i.e., the temperature, steam/coal ratio, and oxygen/coal ratio, were taken from Table 7-1.

The technique employed to compute thermodynamic equilibrium values was based on the EQUICA Program developed by Battelle.(26,27) Detailed results of computed values of trace substances for the various gasifiers using the EQUICA Program are presented in Appendix D. Salient data are summarized in this section.

A comparison of experimental and calculated gas compositions for the Koppers-Totzek gasifier is shown in Table 8-4. The data indicate close agreement on the major gaseous components, namely, CO and H_2. On the other hand, the agreement is poor for CO_2, CH_4, and NH_3. Since experimental values for trace elements are not available, the validity of the computer calculated trace element concentrations cannot be checked. The approach to equilibrium, and hence the validity of the calculated values, is probably reasonably good when the temperature of the equilibrium mixture is above 1000 C (1800 F). Below this temperature, the assumptions of thermodynamic equilibrium and stability may not be valid. Thus, when predicted gaseous compositions for 315 C (600 F) were compared with experimental values for major components (CO, H_2), the deviations were extremely large. This confirms earlier observations (see Figure 8-1) on the predictive power of thermodynamic calculations at temperatures below 1000 C.(27) Insufficient time was available for investigating the causes of these deviations and, when possible, for modifying the program to avoid these difficulties.

The calculated gas compositions are summarized in Table 8-5. The detailed data are presented in Appendix D. It should be noted that these compositions apply to the gas phase only and do not include any fly ash suspended in the gas. Removal of particulate matter is considered

TABLE 8-4. COMPARISON OF PREDICTED AND EXPERIMENTAL K-T GAS COMPOSITION

	Composition at 2700 F, Gasifier Exit	
	Experimental Values	Predicted Values
Concentrations, mole percent		
CO	56.0	60.9
H_2	35.0	38.7
CO_2	7.0	0.3
N_2	1.0	0.5
H_2S	1.0	0.8
COS	0.1	0.08
Concentrations, volume ppm		
CS_2	ND	20
H_2O	1.0	0.73
CH_4	800	0.1
NH_3	1700	1.5
Concentrations, weight ppm		
Fe	ND	2768
K	ND	878
Na	ND	270
SO_2	ND	3
Mg	ND	211
Cu	ND	8
Pb	ND	19
Se	ND	1
Cl_2	ND	-0
Hg	ND	0.112

ND = Not determined.

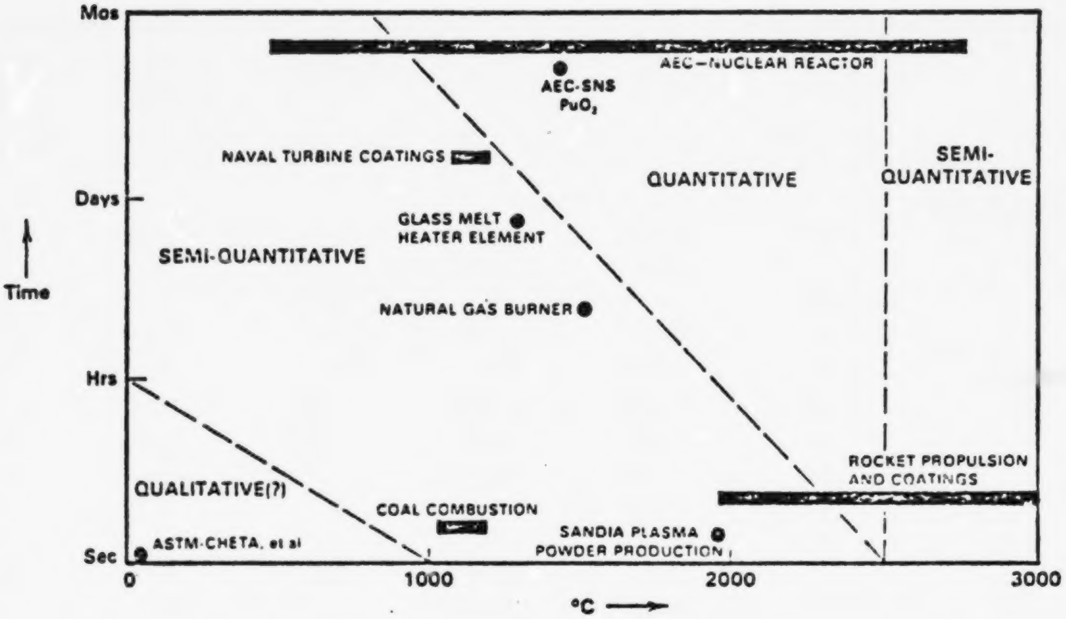


FIGURE 8-1. BATTELLE EXPERIENCE WITH TIME-TEMPERATURE EFFECTS ON PREDICTIVE POWER OF THERMODYNAMIC CALCULATIONS

Note that Coal Combustion and Gasification Processes Fall into the Semiquantitative Estimation Category

Source: Reference 27.

TABLE 8-5. COMPARISON OF THERMODYNAMICALLY PREDICTED TRACE CONSTITUENT DATA

System	Coal-Fired Boiler	K-T Gasifier	K-T Gasifier	Winkler Gasifier	Wellman-Galusha Gasifier	Riley-Morgan Gasifier
Temperature, C (F)	650 (1200)	1815 (3300)	650 (1200)	980 (1800)	650 (1200)	680 (1250)
ppm by weight in gas phase						
H_2S	0	14,292	14,811	19,445	12,352	17,042
COS	0	1,358	2,197	720	587	1,720
SO_2	9,755	3	0	0		
NH_3	0	0.1	5.65	7.0	11.5	11.2
Fe	0	2,768	0	0	0	0
K	0.408	878	898	1,095	697	990
Na	0	270	0.02	336	0.01	0.08
CS_2	0	81	8.3	24	0.3	9.4
Mg	0	212	0	0	0	0
Cu	0	8.3	0	0	0	0
Pb	0	9.5	0.004	5.82	8.6	12.2
Se	0	1.14	1.17	1.43	0.91	1.3
Cl_2	0.098	0.008	0.002	0	0	0
Hg	0.004	0.112	0.115	0.14	0.07	0.10
HgO	0.012	0	0	0	0	0
$HgCl_2$	0.001	0	0	0	0	0
SeO_2	0.231	0	0	0	0	0
P_4O_{10}	12.85	0	0	0.611	71.3	101
As	0	7.7	7.9	9.7	6.1	8.7
$ZrCl_4$	0	0	11.0	0.005	0	0
$BeCl_2$	0	5.1	5.3	2.5	0	0
$TiCl_4$	0	0	303	6.06	0	0
Zn	0	150	0	181	0	0
P	0	39	0	48	0	0
Cd	0	1.38	0	1.64	0	0
Total species present in gas phase	8	19	14	17	11	11

necessary before the gas can be used as a reductant. Data on the composition of the ash also are included in Appendix D. The data in Table 8-5 support the following conclusions:

(1) The flue gas from the coal-fired boiler, after cooling to 650 C (1200 F) contains eight gaseous trace species. This number is lower than that for any of the gasifier products.

(2) Among the gasifier product gases, the general level of trace species is determined primarily by the gasification temperature. The Koppers-Totzek gasifier operating at 1815 C showed 19 trace constituents, the Winkler gasifier operating at 980 C showed 17, and the two lower temperature gasifiers (Wellman-Galusha and Riley-Morgan) operating at 650-680 C showed 11 species.

(3) Cooling the Koppers-Totzek product gas to 650 C (1200 F) and reestablishing equilibrium reduces the number of gaseous trace species to 14. Note that this is still higher than the value for the two gasifiers which operate at this temperature level.

Actually, of course, the gasifier product gas will be cooled below 650 F during the cleanup steps, and hence the gaseous trace constituent concentrations will be less than the values shown in Table 8-5. If no gaseous species have to be removed but only fly ash, a high-temperature, high-efficiency electrostatic precipitator can be used. This can be done at a temperature of about 430 C (800 F), thus eliminating the need for reheating the gas prior to using it as a reductant. In the more likely case that gaseous species such as NH_3 have to be removed, the gas will have to be scrubbed with water. This will require reheating the gas but will result in even lower trace constituent concentrations in the gas, since equilibrium will then be established (or at least approached) at a much lower temperature (about 50 C) and some species will be at least partially soluble in the water.

8.3 Contacts with Process Vendors

The developers and/or vendors of several sulfur-producing FGD and related processes were contacted to obtain their opinions regarding the effects of trace components in coal-based reducing gases upon their systems. The processes considered included the Peabody Citrex process, IFP Catalytic NH_3 scrubbing process, and the American Smelting and Refining Company (ASARCO) reduction process. The individuals contacted felt that the trace components should not present any problems since: (1) the proportion of the trace substances introduced by the coal gas is only about 3.6 percent of the main boiler flue gas constituents and (2) the small volume of the gas generated will be thoroughly scrubbed to give near zero levels of particulate matter and most gas phase contaminants. One purpose of the thermodynamic calculations was to examine if there was a theoretical basis for the assumption of near complete removal of trace elements in the coal gas by liquid scrubbing to near ambient temperatures. This purpose was not completely achieved because of the difficulties encountered with the lower temperature calculations.

9. EFFECT OF TRACE CONSTITUENTS ON FGD SYSTEMS

In Section 7, several coal gasification processes were discussed. In Section 8, the trace contaminants present in the producer gas were examined. In this section the effect of the coal gas trace contaminants on the FGD processes proper and on the subsequent SO_2 reduction catalysts will be evaluated.

9.1 Overall FGD Plus Reduction Systems

To understand the effect of trace elements on the FGD chemistry, a knowledge of both the overall sulfur-producing conceptual systems and the chemistry of the important steps which utilize the coal-based reducing gas will be useful. The possible routes to sulfur production employing various FGD processes and subsequent reduction processes are described in Figure 9-1. The reduction processes include: (1) the Claus sulfur plant, (2) the ASARCO-Phelps Dodge direct sulfur process, and (3) the liquid Claus unit.

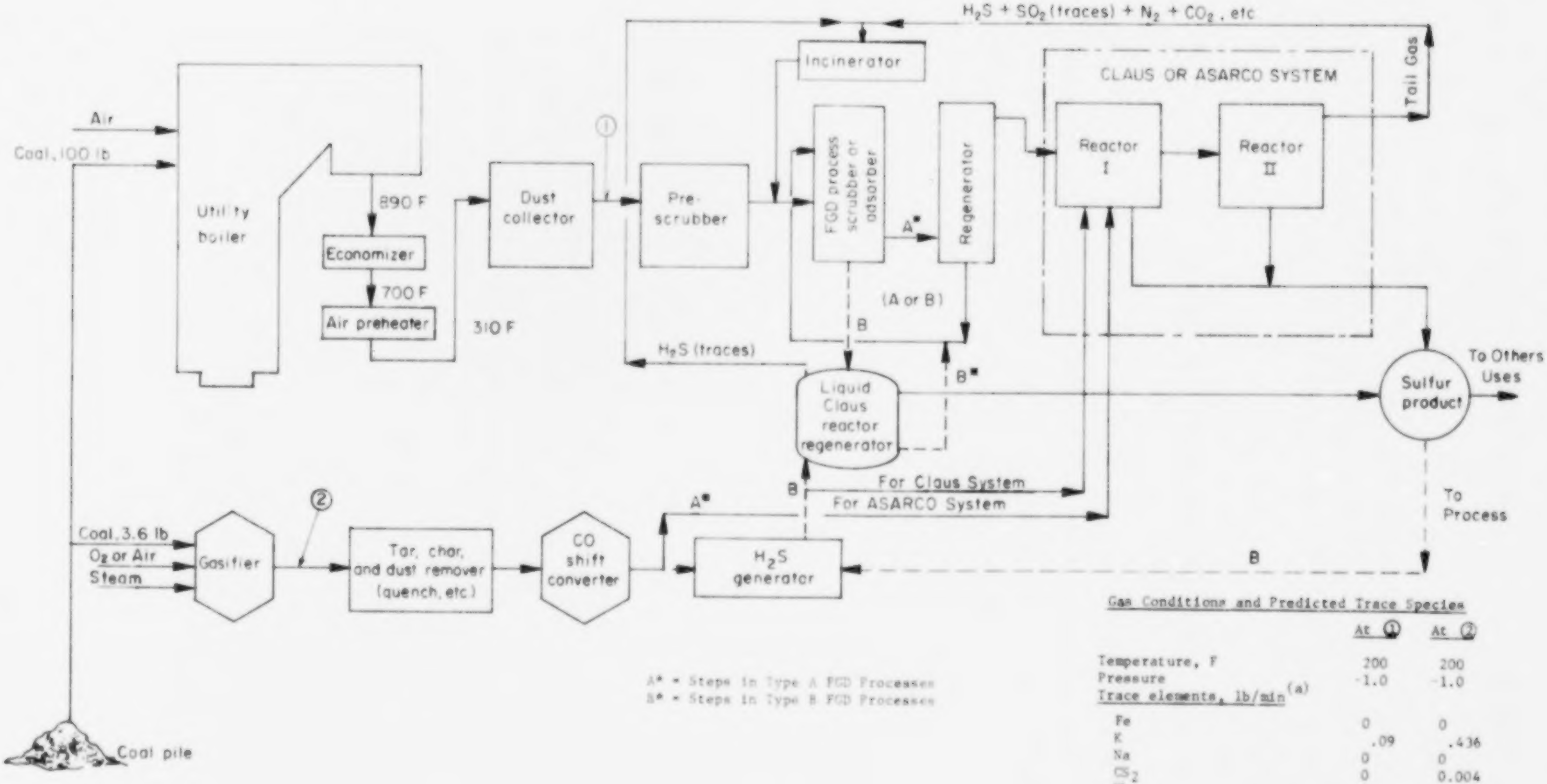
9.2 Effects on FGD Processes

An analysis of the data shown in Figure 9-1 indicates that:

(1) 3.6 pounds of coal will be fed to the coal gasifier for each 100 pounds of coal fed to boiler for generating steam. Thus, even if the trace species volatilization rate is assumed equal for the gasifier and boiler, the gasifier will introduce only 3.6 percent of the trace species which will be introduced into the FGD system via the boiler flue gases.

(2) Prescrubbing of boiler flue gas with water is a desirable step to eliminate all condensible and soluble trace species at a temperature of 30-50 C (90-120 F). Whether water prescrubbing will reduce also the trace species in gaseous state, and if so, to what degree has not been quantified experimentally.

(3) The FGD scrubber handles 144 volumes of flue gas from boiler for every volume of reducing gas entering the process from the gasifier.



Air
Coal, 100 lb
Utility boiler
890 F
Economizer
700 F
Air preheater
310 F
Dust collector
①
Pre-scrubber
Incinerator
FGD process scrubber or adsorber
A*
Regenerator
(A or B)
B
B*
H₂S (traces)
Liquid Claus reactor regenerator
$H_2S + SO_2$ (traces) + N_2 + CO_2, etc
CLAUS OR ASARCO SYSTEM
Reactor I
Reactor II
Tail Gas
Sulfur product
To Others Uses
To Process
B
Coal, 3.6 lb
O_2 or Air
Steam
Gasifier
②
Tar, char, and dust remover (quench, etc)
CO shift converter
A*
B
For Claus System
For ASARCO System
H₂S generator
Coal pile

A* = Steps in Type A FGD Processes
B* = Steps in Type B FGD Processes

FIGURE 9-1. POSSIBLE ROUTES TO SULFUR PRODUCTION BASED ON COAL GASIFICATION REDUCING GAS IN FGD PROCESSES

(Schematic of the Overall FGD Process System)

Gas Conditions and Predicted Trace Species

	At ①	At ②
Temperature, F	200	200
Pressure	-1.0	-1.0
Trace elements, lb/min[(a)]		
Fe	0	0
K	.09	.436
Na	0	0
CS_2	0	0.004
Pb	0	0.005
Se	0	-0
Cl_2	.02	0
Hg	.0009	-0
HgO	.0026	0
SeO_2	.051	0
P_2O_5	2.83	0.04
As	0	0.004

(a) For a 1000-MW plant burning 406 ton/hr (13,540 lb/min) coal.

Thus, it appears reasonable to estimate that the effect of trace species in the reducing gas on the FGD scrubbing system itself will be inconsequential. However, special consideration must be given to FGD processes which require a reductant for some purpose in addition to that needed for reducing the SO_2. This is the case for the Shell FGD process and the Catalytic-IFP NH_3 scrubbing process. The Shell process requires a reductant to regenerate the $CuSO_4$ and thereby liberate the SO_2. Shell recommends hydrogen for this purpose. The Catalytic-IFP process requires a reductant for its sulfate reduction reactor. For such purposes it would be convenient to obtain both reductants from the coal. If this is to be done, consideration must be given to the effects of trace contaminants from the coal upon the portion of the FGD process where the reductant is introduced. An important consideration is the extent to which trace constituents are already present at the location in question by transfer from the flue gas. One would not expect problems in the Shell process because the copper-containing sorbent is periodically contacted with the flue gas. In the Catalytic-IFP process, the extent to which impurities in the flue gas reach the sulfate reduction reactor is not well defined.

9.3 Effects on Sulfur Production Processes

As shown in Figure 9-1, there are three processes in which the sulfur dioxide stream concentrated by the Type A FGD processes can be converted to elemental sulfur. Two of these, commercially proven and in use for at least a decade, are

(1) The vapor-phase Claus sulfur plant
(2) The liquid-phase Claus reactor.

The basis of both these processes is the reaction:

$$SO_2 + 2H_2S \rightarrow 3/2\ S_2 + 2H_2O,$$

which indicates gaseous H_2S to be a requirement. The third process does not need gaseous H_2S and can use the coal gas directly according to the following vapor-phase reaction:

$$1.5\ SO_2(g) + CO + 2H_2 \rightarrow 0.75\ S_2(g) + CO_2(g) + 2H_2O.$$

This reaction is representative of the ASARCO-Phelps Dodge process. A pilot plant with a sulfur production capacity of 20 tons/day has been in operation at ASARCO's El Paso, Texas, smelter since August, 1971.(9,10) However, the process employs reformed natural gas (containing CO and H_2) rather than coal gas. The reformed natural gas is generated by the Phelps Dodge Reforming process.(28) In these processes, the common unknown is the technical feasibility of using coal gas in place of reformed natural gas. Conversations with ASARCO and others have indicated that experimental studies in this area are under way; no data are available yet. Also, there is a reluctance to sharing of available information since proprietary interests are involved. In this section, a critical analysis of the effect of coal gas trace constituents on the three processes listed above will be attempted.

Vapor-Phase Claus Reaction

In this process a stoichiometric mixture of SO_2 and H_2S is reacted over a bauxite catalyst at 230-400 C (450-750 F) and atmospheric pressure as follows:

$$SO_2 + 2H_2S \rightarrow 3/2\ S_2 + 2H_2O.$$

The reactor inlet temperature is restricted to about 230 C (450 F) because the reaction is exothermic and the equilibria are less favorable at higher temperatures. The catalyst performance is unaffected by the presence of CO_2. However, any ammonia and hydrocarbons must be removed from the feed, since these species are detrimental to the catalyst. The sulfur vapor is condensed at about 150 C (300 F).

According to a H_2S production process vendor coal gas can be converted to H_2S to provide the following product composition as predicted by thermodynamics:(29)

	Coal Gasifier Product, mole percent dry
CO	50
H_2	34
CO_2	14
CH_4	1
N_2	1

	H_2S Generator Product, mole percent dry
H_2S	55.7
SO_2	0.3
CO_2	40.4
COS	1.8
CS_2	0.3
CO	0.4
N_2	0.7
H_2	0.4

Thus, the product gas exiting at 430-540 C (800-1000 F) can be fed directly to the Claus converter in admixture with the SO_2 from the FGD processes. The trace species in the coal gasifier product entering the H_2S generator can be assumed to be too small to cause problems of catalyst poisoning; the gas cleanup (scrubbing and high efficiency particulate matter removal) will have removed over 98 percent of gaseous and condensed trace species as discussed in Section 8. However, the CO and traces of methane can result in the following undesirable reactions in the Claus reactor:

$$CH_4 + SO_2 \rightarrow COS + H_2O + H_2$$

$$CO + S \rightarrow COS$$

$$CO_2 + H_2S \rightarrow COS + H_2O$$

$$CH_4 + 2S_2 \rightarrow CS_2 + 2H_2S$$

$$CO + S_2 \rightarrow CS_2 + 1/2\ O_2.$$

The CS_2 and COS thus produced can be burned in the tail gas incinerator to SO_2 and recycled to the FGD scrubber. Any trace species in the incinerator gas with tendency to augment oxidation of the scrubbing liquor in the FGD absorber will be minor. The oxidation products are handled as a purge stream which already exists in the parent FGD process. These discussions indicate that a coal gasifier product can be employed to replace other sources of reducing gas for a Claus sulfur plant.

Liquid-Phase Claus Processes

In the Citrate, Phosphate, and Catalytic-IFP processes, the SO_2-laden absorber liquor is reacted with an H_2S-rich gas stream in a two- or three-stage liquid reactor system.* Available data indicate that catalysts are not employed in these processes. Therefore, potential catalyst poisoning problems due to trace species in coal gas do not arise. However, catalysts are utilized in the H_2S generation and SO_3 reduction steps.

For these processes, there is no experimental evidence regarding the effects of using a coal gasifier-based H_2S stream. The following information provided by Peabody Engineered Systems (CITREX process vendor) and Catalytic, Inc., (Catalytic-IFP process vendor) may be helpful.

- Water washing of the coal gas should eliminate nearly all trace species having a potential to cause adverse effects on sulfur production steps.
- The CO_2, CS_2, and NH_3 in the H_2S gas do not adversely affect the catalyst or the liquid Claus process
- A high COS concentration in the H_2S feed gas will result in an undisclosed adverse reaction in the liquid Claus step. The degree of adversity is not quantified.
- Apparently, for the citrate process removal of CO_2 from the shift converter gas with at least a single stage CO_2 removal step (e.g., the hot carbonate process) is desirable. This will provide to the H_2S generator a feed rich in H_2 and low in CO and COS. The net result is an H_2S stream with >80 mole percent H_2S content, which insures high sulfur conversion efficiency and high-quality sulfur product. Reportedly, the Catalytic-IFP process seems to have the advantage of utilizing the coal gasifier product directly without a shift converter.
- According to Catalytic, Inc., the impurities contained in the coal gas stream may build up on the H_2S generator catalyst but may not poison it. Thus, periodic washing of the catalyst bed is provided for by installing a spare catalyst chamber in the Catalytic-IFP process design.

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* The Catalytic-IFP liquid Claus unit is a single-stage system which accomplishes essentially 100 percent conversion to bright commercial grade elemental sulfur in a single pass.

Discussions with the various vendors suggest that a system for coal gasification, cleanup, and H_2S generation shown in Figure 9-2 would be necessary. Since the gas necessarily is cooled both before and after the shift reactor, it would probably be advisable to use a low temperature shift catalyst to minimize the extent of gas reheating. Shift catalysts are now available which can be used at temperatures of 200-250 C (390-480 F) and can tolerate reasonable concentrations of H_2S without poisoning. The choice is not obvious, however, because the high temperature shift catalysts have the advantage that they effect nearly complete hydrolysis of COS to form H_2S, thereby eliminating an undesirable specie in the product gas.

Based on the available information and best judgment, the effect of trace species on the liquid Claus reactions is expected to be a minor problem in comparison with the other problems of successfully operating a regenerative FGD system. The magnitude of the problems of utilizing coal-based reducing gas can only be judged accurately by conducting experimental tests with various coals and FGD processes.

ASARCO Direct Sulfur Process

The ASARCO process for reducing SO_2 to sulfur with H_2/CO was discussed in Section 5. A flow sheet of this process as adapted for use with coal gas is shown in Figure 9-3. Reportedly, the technical feasibility of the process has been proved in a 20 ton/day pilot plant operating since 1971 on smelter gas and using reformed natural gas as the reductant.(10) The requirement of the process is that the feed have at least 12 mole percent SO_2. This is easily met by all the Type A FGD processes, since these processes produce streams containing 20 to 85 percent SO_2.

As shown in Figure 9-3, the process employs two catalytic reactors, the second of which is a Claus reactor. The type of catalyst in primary reactor is proprietary information. Probably, the secondary reactor contains bauxite or alumina as the Claus catalyst. We have already noted that trace species in coal gas, if properly scrubbed, will not harm the Claus catalyst. However, since no information on the primary

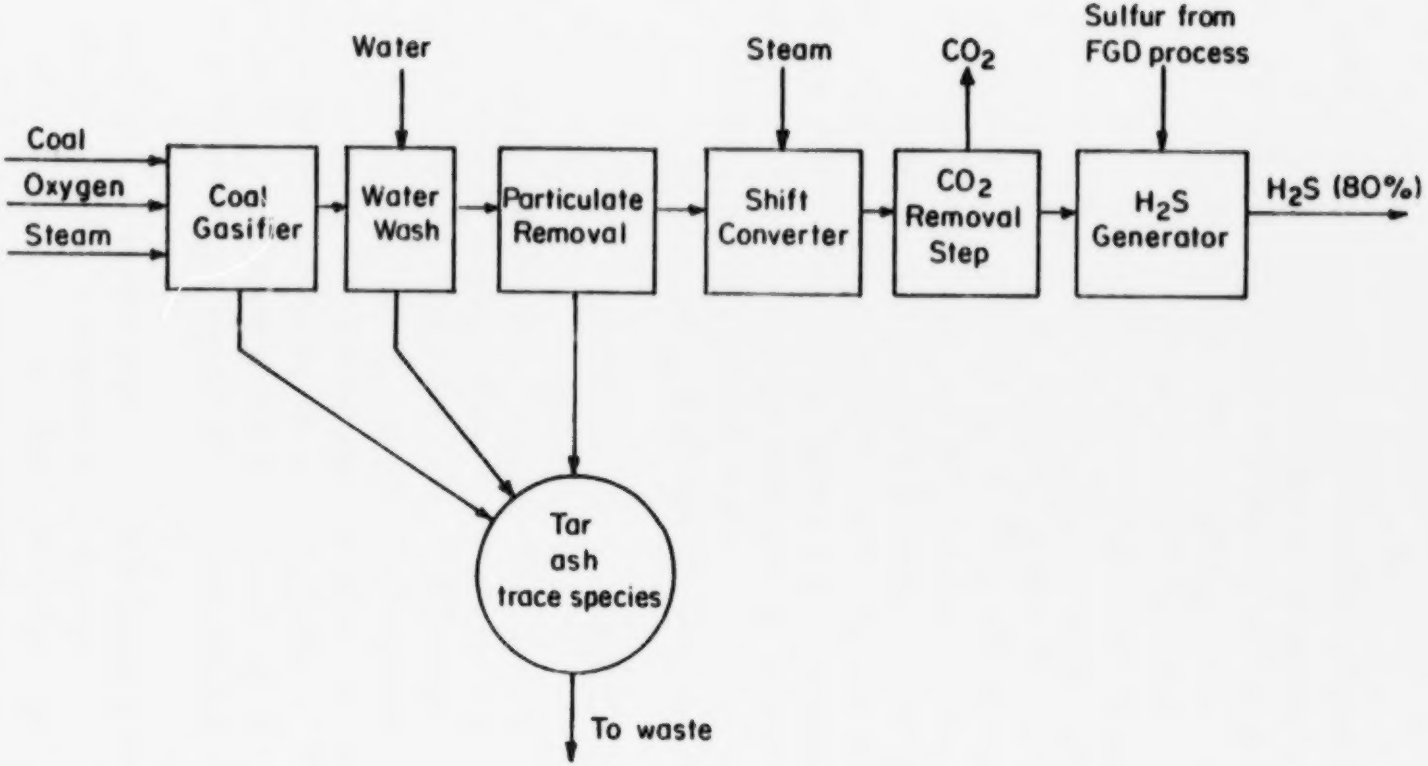

Coal
Oxygen
Steam
Coal Gasifier
Water
Water Wash
Particulate Removal
Steam
Shift Converter
CO_2
CO_2 Removal Step
Sulfur from FGD process
H_2S Generator
H_2S (80%)
Tar ash trace species
To waste

FIGURE 9-2. SCHEMATIC FOR COAL GASIFICATION, CLEANUP, AND H_2S GENERATION

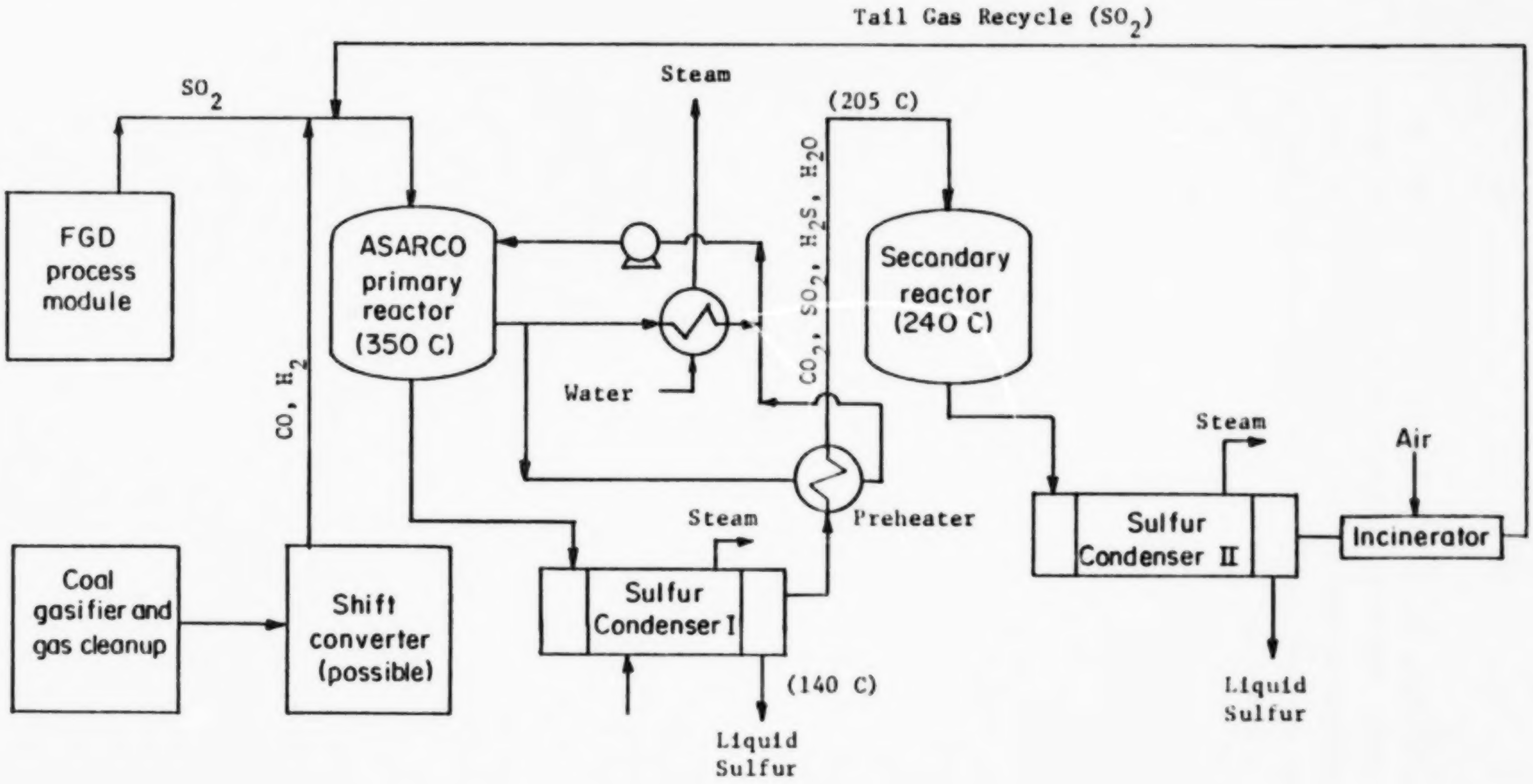

Tail Gas Recycle (SO_2)
SO_2
FGD process module
Coal gasifier and gas cleanup
Shift converter (possible)
CO, H_2
ASARCO primary reactor (350 C)
Steam
Water
CO_2, SO_2, H_2S, H_2O
(205 C)
Secondary reactor (240 C)
Preheater
Steam
Sulfur Condenser I
(140 C)
Liquid Sulfur
Steam
Sulfur Condenser II
Liquid Sulfur
Air
Incinerator

FIGURE 9-3. SCHEMATIC OF AMERICAN SMELTING & REFINING COMPANY (ASARCO) ELEMENTAL SULFUR PRODUCTION PLANT ADAPTED TO USE OF COAL GAS

reactor catalyst is available, the effect of trace species in coal gas on it cannot be evaluated. ASARCO is studying the feasibility of substituting coal gas for reformed natural gas. If the initial work in this area is promising, more specific studies of the effects of trace species on the process could be conducted.

10. GAS CLEANUP SYSTEMS

Previous sections of this report (and Appendix C) have presented information on gasification systems and their products. It is clear from the discussion of Section 9 that the raw gas from a gasification system will have to be washed with water before it can be used as a reducing gas in the manner intended in this report. This water washing will remove principally particulate matter, ammonia, and hydrogen cyanide. The purpose of this section is to discuss possible water washing systems and to examine the effectiveness of such systems in removing ammonia and hydrogen cyanide from gases. Additional information on these subjects is presented in Appendix E.

10.1 Scrubber Systems

A number of water scrubbing systems have been proposed for use with coal or oil gasification processes. These are discussed in Appendix E. A frequent omission in these conceptual systems is that of providing no means for removing the absorbed gaseous species, primarily ammonia, from the scrubbing liquor. Without such removal, the ammonia concentration would be expected to build up to some steady-state concentration in the scrubbing liquor loop and, from that time on, there would be little change in ammonia concentration in the gas phase through the scrubber. Of course, the particulate matter must also be removed from the scrubbing liquor.

A conceptual design for a spray scrubber which would remove gaseous impurities as well as particulate matter and tars is shown in Figure 10-1. The water loop would be provided with a separator, settler, and/or filter to remove tars, tar oils, naphtha, and particulate matter and then a rectification-stripping column to drive off the absorbed materials and soluble materials more volatile than water. Subsequent to the stripping column, a water cooler would reduce the water temperature to a level suitable for use in the spray scrubber. A water purge and water makeup also are indicated.

A key feature in this conceptual design is the configuration of the rectification-stripping column. By using closed steam heating of the reboiler, additional water is not added to the water loop unnecessarily. Also, provision for a rectification section permits the recovery of materials, such as ammonia, which may have some value and prevents environmental contamination through indiscriminate discharge of these materials to the atmosphere.

10.2 Effectiveness of Scrubber Systems

The conceptual gas cleanup system shown in Figure 10-1 includes a spray scrubber, because this type of equipment can handle a solids-laden gas while still providing reasonably good gas-liquid contacting. The mass transfer characteristics of a spray tower are not so favorable as those of a packed tower or tray tower, but the latter type of equipment would readily be plugged by the particulate matter contained in the raw gasifier gas. The maximum number of mass transfer units achievable in a spray tower is about three. Therefore, some calculations were made to determine the removals of gaseous species that could be obtained with three mass transfer units. The results indicate that up to 93 percent of the ammonia (NH_3) and 85 percent of the hydrogen cyanide (HCN) can be removed from a typical raw coal gas by water scrubbing at 30 C. A substantial fraction of the hydrogen sulfide (H_2S) in the gas will also be removed.

A few exploratory calculations were performed on the stripping of absorbed gases back out of the water. Ammonia can easily be stripped from the water; less than two equivalent plates would be required to reduce the ammonia concentration in the water to 1 ppm.

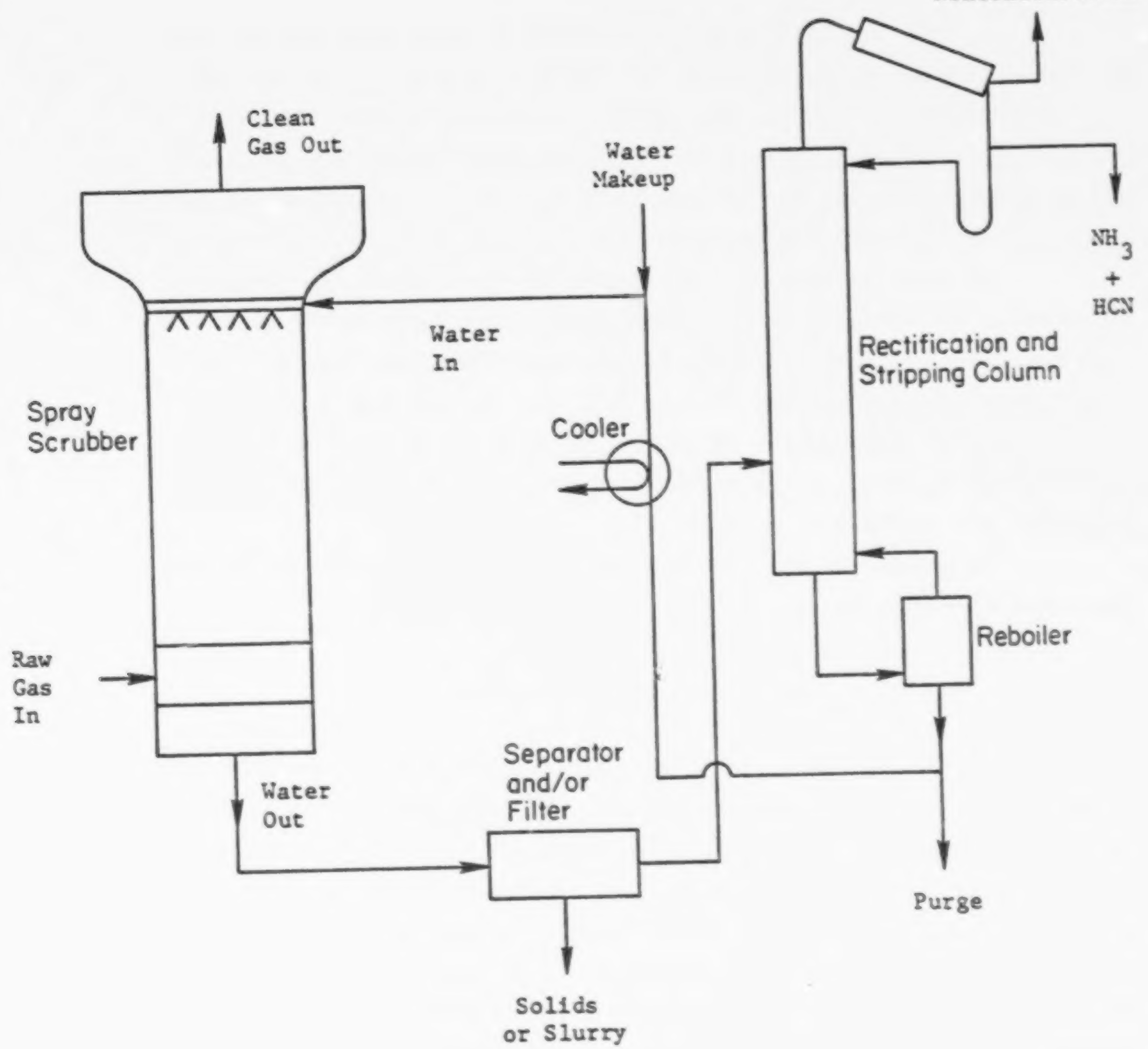

Noncondensibles
Clean Gas Out
Water Makeup
NH_3 + HCN
Water In
Rectification and Stripping Column
Spray Scrubber
Cooler
Reboiler
Raw Gas In
Separator and/or Filter
Water Out
Purge
Solids or Slurry

FIGURE 10-1. CONCEPTUAL DESIGN OF A SPRAY SCRUBBER, GAS CLEANUP SYSTEM

11. COSTS OF GASIFIER-BASED REDUCTANT SYSTEMS FOR FGD PROCESSES

In this section the costs of gasifier-based reductant systems for FGD processes are considered. It should be recognized at the outset that these costs are necessarily rather approximate because they apply to systems that are still only conjectural. Detailed system designs have not been made and could not be accurately made at this time because some questions on the technology involved have not yet been answered.

In order to make the cost estimates as realistic as possible, segments of the systems such as oxygen plants and Claus plants were costed as complete units based on current cost data from vendors. Additional detail on the sources of cost data and how these data were used is presented in Appendix G. Additional details on the engineering calculations involved in the system designs (i.e., material and energy balances) are included in Appendix F.

In the following, the application of reductant systems to the two types of FGD processes will be considered separately.

11.1 Type A FGD Processes

The Type A FGD processes can use a H_2/CO mixture for reduction of the concentrated SO_2 stream produced. The most desirable way to accomplish this would be with a system similar to the ASARCO process. This involves a two-stage reaction system with some sulfur produced in both reactors. The first reduction reactor contains the ASARCO catalyst and the second reactor a Claus catalyst. It is possible that a third reactor containing Claus catalyst might be necessary if 95 percent sulfur recovery is to be achieved. In this case, the reduction system would actually contain a two-stage Claus plant and would, in effect, be very similar to a three-stage Claus plant overall. The only difference is that a different catalyst would be used in the first stage so that a H_2/CO mixture could be fed instead of H_2S.

On the other hand, a reductant system for Type A FGD processes is not entirely dependent upon the ASARCO technology because a standard cobalt-molybdenum hydrogenation catalyst could be used in the first stage. The only disadvantage of this is that the first reactor would then produce only H_2S and no sulfur would be removed at this point. As far as the system cost is concerned, it should make little difference which type of catalyst is used in the first reactor. In either case the reduction system should be very similar in cost to a three-stage Claus plant. Any differences in reactor size (space velocity) or catalyst cost would be unknown at this time anyway.

The cases considered in this section include both oxygen- and air-blown gasifiers and both classes of Type A FGD processes, i.e., those which produce an 85 percent SO_2 stream and those which produce a 25 percent SO_2 stream. Thus, four different levels of gas dilution are included.

Material Balances

The reducing gas compositions used in the material balance calculations are shown in Table 11-1. The oxygen-blown case is based on a Koppers-Totzek gasifier and the air-blown case on a Wellman-Galusha, although other gasifiers would give similar compositions.

The material balance flow sheets for the four cases are presented in Figures 11-1 through 11-4. The first two figures are for oxygen-blown gasifiers and the second two are for air-blown gasifiers. In these figures the SO_2 reduction system is shown as consisting of two stages with the second being a Claus reactor. As mentioned previously, there will probably be in fact two separate Claus reactors, and the costs have been developed to reflect this. It is assumed that no shifting of CO to H_2 is required before the first reduction step.

Investments

The estimated investments for reduction systems for 1000-MW and 500-MW power plants are presented in Tables 11-2 and 11-3, respectively. In addition to the four cases based on coal gasification, two cases are shown for the Allied SO_2 reduction process, which uses natural gas as the reductant. The investments for the coal gasifier-based systems are consistently greater than those for the Allied process.

TABLE 11-1. REDUCING GAS COMPOSITIONS USED IN MATERIAL BALANCE CALCULATIONS

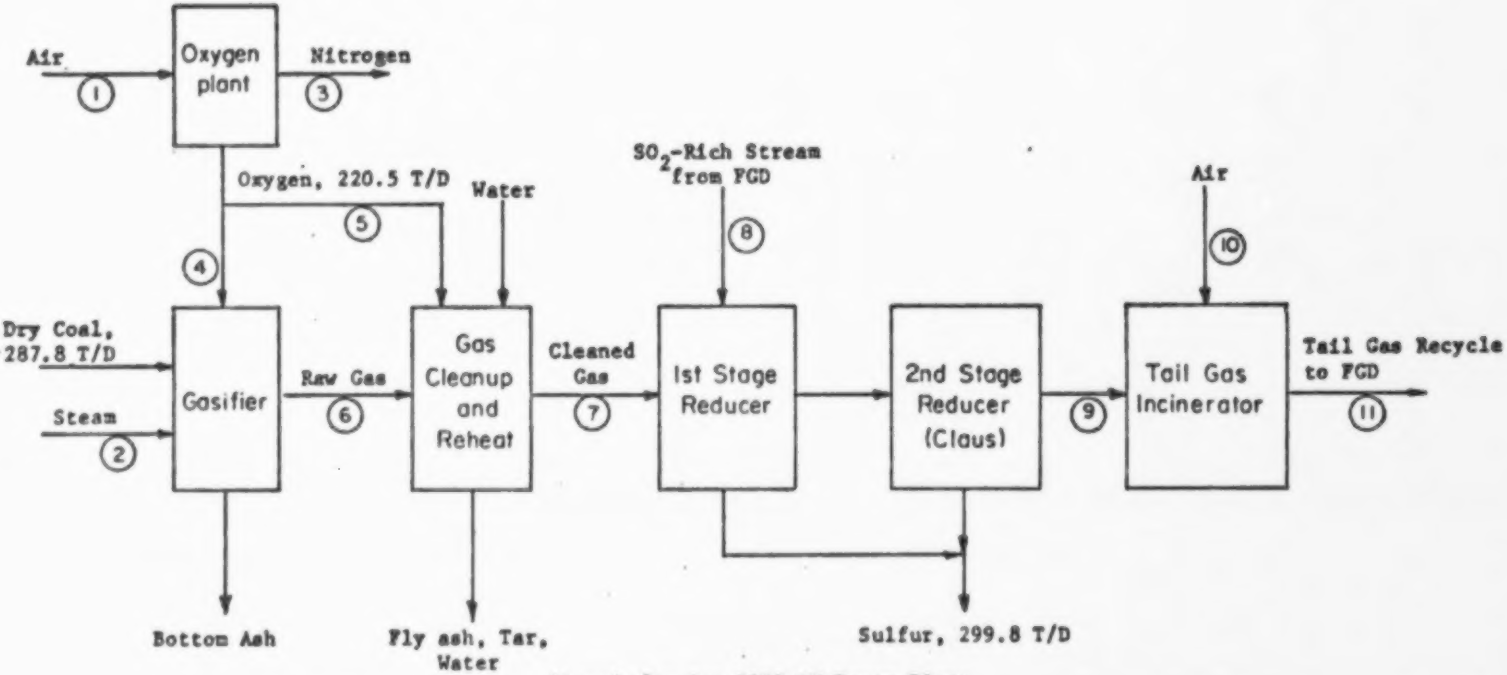
	Concentration (mole % except as otherwise noted)			
	Oxygen-Blown Gasifier (Koppers-Totzek)		Air Blown Gasifier (Wellman Galusha)	
Specie	Leaving Heat Recovery System(a)	Leaving Water Wash(b)	Leaving Heat Recovery System(c)	Leaving Water Wash(b)
H_2	24.43	30.65	13.32	13.18
CO	39.08	49.03	25.39	25.11
CO_2	4.97	6.24	3.02	2.99
CH_4	0.08	0.10	2.40	2.37
H_2S	0.92	1.06	0.54	0.49
COS	0.08	0.10	0.02	0.02
NH_3	0.17	0.01	0.50	0.01
HCN	0.03	--	0.01	--
N_2	0.71	0.89	44.65	44.16
Ar	0.32	0.40	0.15	0.15
H_2O	29.19	11.52	10.00	11.52
	100.00	100.00	100.00	100.00
Tar, grains/scf	--		3.82	
Particulate matter, grains/ scf	11.57 11.57		0.1-0.5 0.1-0.5	

(a) From data on Illinois coal (Table C-1) after adjustment to 3.5 percent S coal and addition of H_2O, NH_3, Ar, CH_4, and HCN from Reference 19.

(b) Based on reduction of NH_3 to 100 ppm, high removal of HCN, 8 percent removal of H_2S, and saturation with water at 120 F and 1 atm.

(c) From data on bituminous coal (Table C-2) after addition of H_2O (assumed conc), H_2S, COS, Ar, and HCN (adjusted from oxygen-blown data), and NH_3.

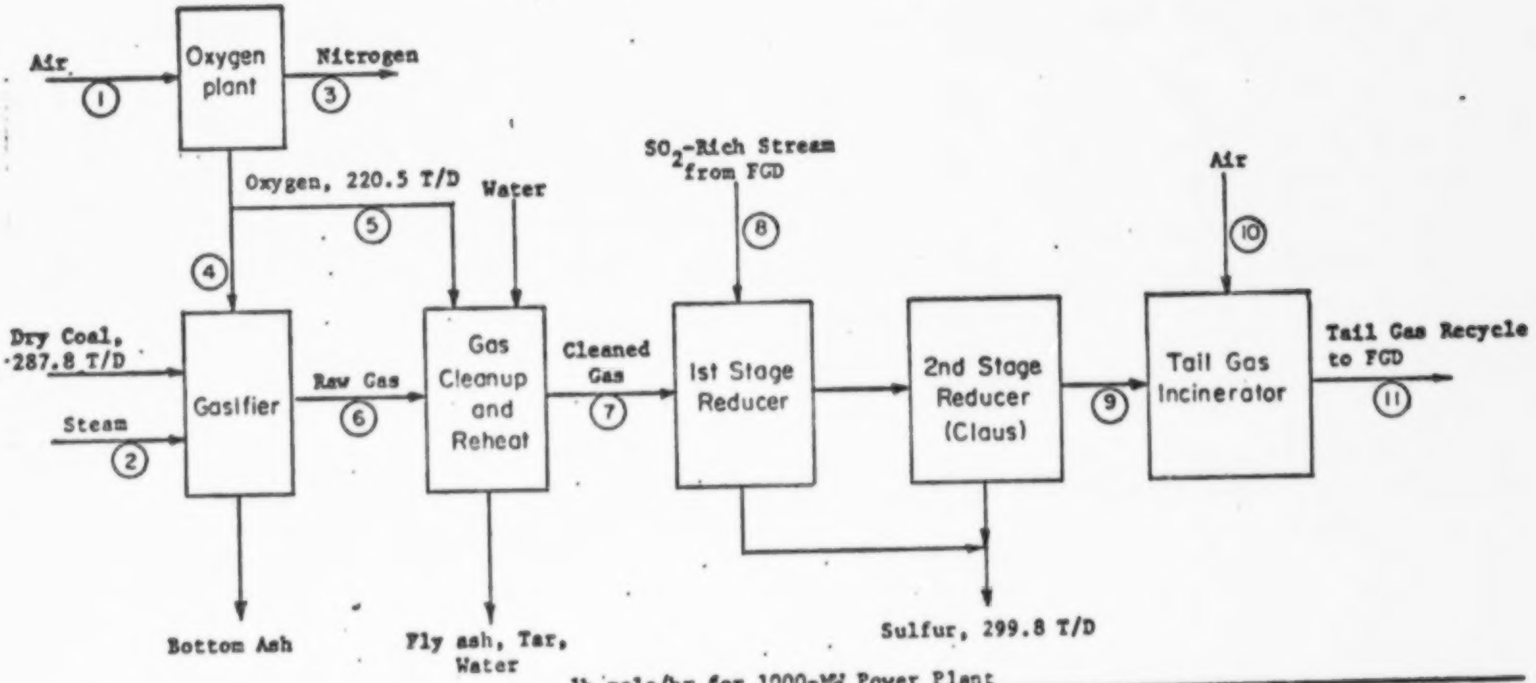
Note: grams/std m^3 = 2.288 (grains/scf).


Air
①
Oxygen plant
Nitrogen
③
Oxygen, 220.5 T/D
⑤
Water
④
Dry Coal, 287.8 T/D
Steam
②
Gasifier
Raw Gas
⑥
Gas Cleanup and Reheat
Cleaned Gas
⑦
SO_2-Rich Stream from FGD
⑧
1st Stage Reducer
2nd Stage Reducer (Claus)
⑨
Air
⑩
Tail Gas Incinerator
Tail Gas Recycle to FGD
⑪
Bottom Ash
Fly ash, Tar, Water
Sulfur, 299.8 T/D

lb mole/hr for 1000-MW Power Plant

Specie	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪
H_2						706.2	674.4		97.8		0.
CO						1129.6	1078.8		156.5		0.
CO_2						143.8	194.7		1117.0		1275.8
CH_4						2.4	2.3		2.3		0.
H_2S						26.6	23.3		3.4		0.
SO_2							1.1	798.3	40.0		43.4
N_2	2643.6		2632.1	10.6	0.9	20.5	21.4		21.4	550.7	572.1
H_2O		360.3				843.7	297.5	140.9	1034.9		1140.7
O_2	702.7		138.5	518.4	45.8		4.1		4.1	146.4	13.6
Other						17.3	11.8		11.8		11.8
Total	3346.3	360.3	2770.6	529.0	46.7	2890.1	2309.4	939.2	2489.2	697.1	3057.4
Temperature, C	27	121			27	177	343	27	288	27	
Temperature, F	80	250			80	350	650	80	550	80	

FIGURE 11-1. MATERIAL BALANCE FLOW SHEET FOR TYPE A FGD, 85% SO_2 STREAM, OXYGEN-BLOWN GASIFIER

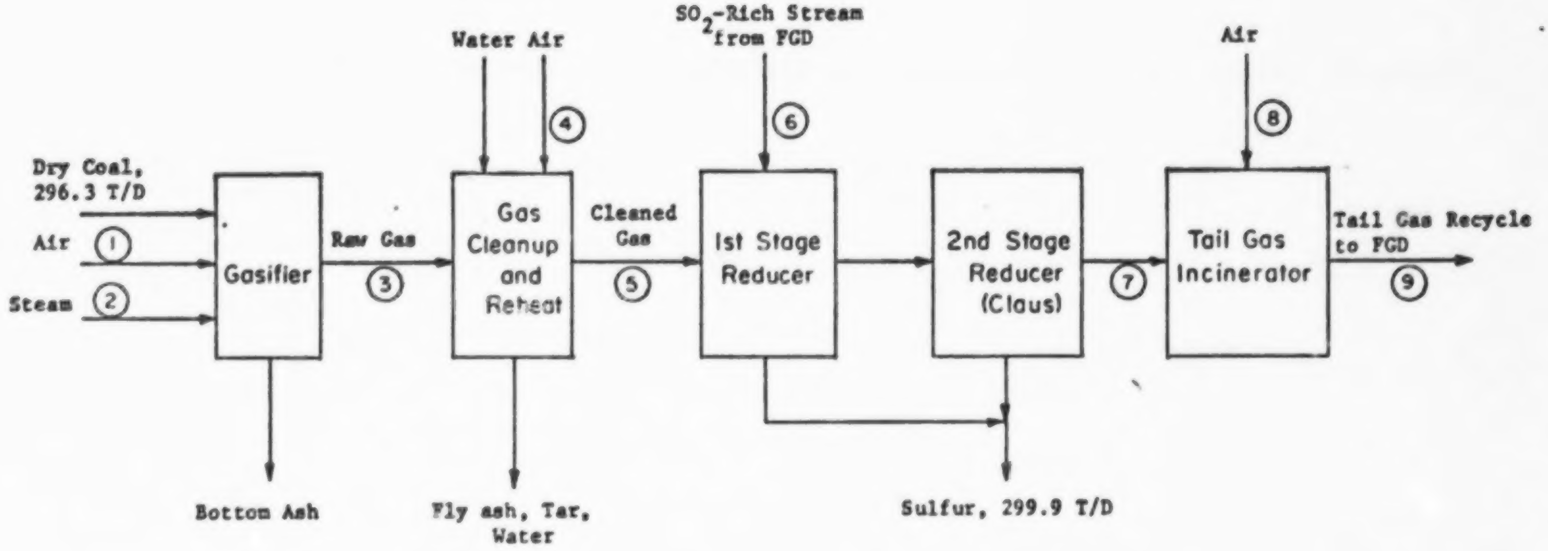


Air
①
Oxygen plant
Nitrogen
③
Oxygen, 220.5 T/D
⑤
Water
④
Dry Coal, 287.8 T/D
Steam
②
Gasifier
Raw Gas
⑥
Gas Cleanup and Reheat
Cleaned Gas
⑦
SO2-Rich Stream from FGD
⑧
1st Stage Reducer
2nd Stage Reducer (Claus)
⑨
Air
⑩
Tail Gas Incinerator
Tail Gas Recycle to FGD
⑪
Bottom Ash
Fly ash, Tar, Water
Sulfur, 299.8 T/D

lb mole/hr for 1000-MW Power Plant

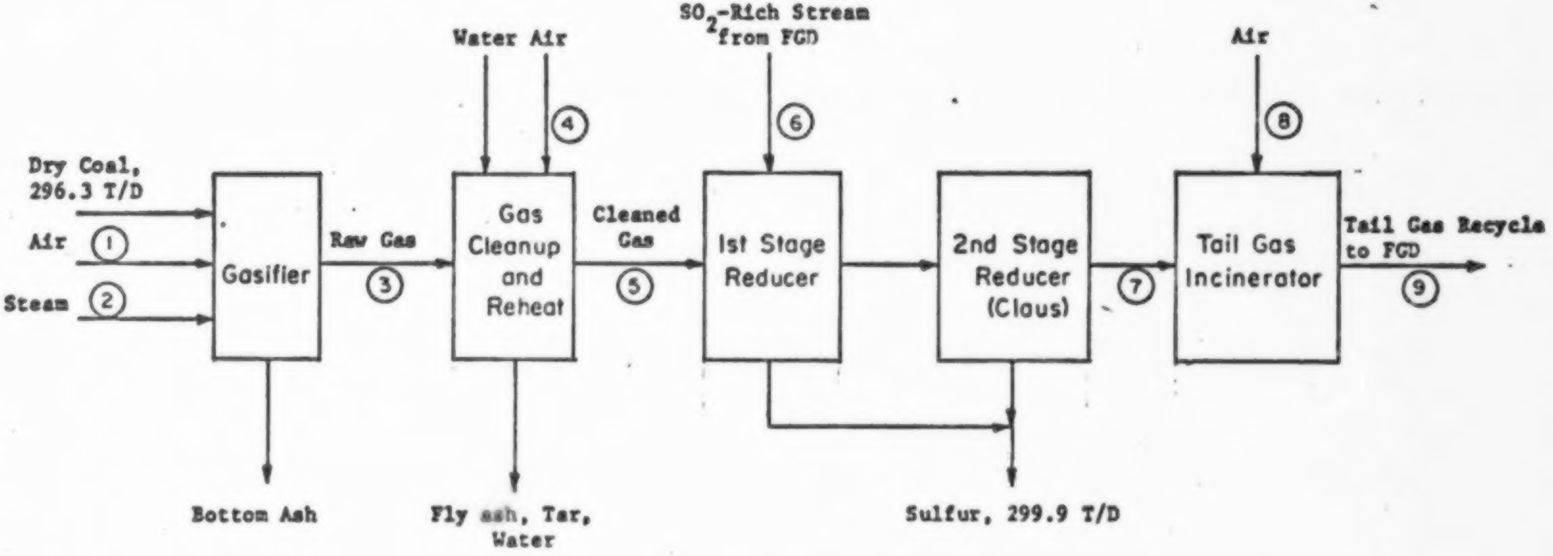
Specie	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪
H_2						706.2	674.4		97.8		0.
CO						1129.6	1078.8		156.5		0.
CO_2						143.8	194.7	542.8	1659.0		1818.6
CH_4						2.4	2.3		2.3		0.
H_2S						26.6	23.3		3.4		0.
SO_2							1.1	798.3	40.0		43.4
N_2	2643.6		2632.1	10.6	0.9	20.5	21.4	1373.1	1394.5	550.7	1945.2
H_2O		360.3				843.7	297.5	479.0	1373.0	550.7	1478.8
O_2	702.7		138.5	518.4	45.8		4.1		4.1	146.4	13.6
Other						17.3	11.8		11.8		11.8
Total	3346.3	360.3	2770.6	529.0	46.7	2890.1	2309.4	3192.2	4743.2	697.1	5311.4
Temperature, C	27	121			27	177	343	27	288	27	
Temperature, F	80	250			80	350	650	80	550	80	

FIGURE 11-2. MATERIAL BALANCE FLOW SHEET FOR TYPE A FGD, 25% SO_2 STREAM, OXYGEN-BLOWN GASIFIER


Dry Coal, 296.3 T/D
Air ①
Steam ②
Gasifier
Raw Gas ③
Water Air
④
Gas Cleanup and Reheat
Cleaned Gas ⑤
SO_2-Rich Stream from FGD
⑥
1st Stage Reducer
2nd Stage Reducer (Claus)
⑦
Air
⑧
Tail Gas Incinerator
Tail Gas Recycle to FGD
⑨
Bottom Ash
Fly ash, Tar, Water
Sulfur, 299.9 T/D

	lb mole/hr for 1000-MW Power Plant								
Specie	①	②	③	④	⑤	⑥	⑦	⑧	⑨
H_2			661.6		604.4		87.6		0.
CO			1260.5		1151.5		167.0		0.
CO_2			150.2		269.6		1254.1		1529.5
CH_4			118.7		108.4		108.4		0.
H_2S			26.8		22.6		3.3		0.
SO_2					2.0	798.3	40.0		43.3
N_2	2205.2		2205.2	471.8	2677.0		2677.0	1401.7	4078.7
H_2O		548.3	496.5		656.1	140.9	1333.1		1640.8
O_2	586.2			125.4	11.4		11.4	372.6	35.0
Other			33.8		9.4		9.0		9.0
Total	2791.4	548.3	4953.3	597.2	5512.0	939.2	5690.9	1774.3	7336.3
Temperature, C	27	121	177	27	343	27	288	27	
Temperature, F	80	250	350	80	650	80	550	80	

FIGURE 11-3. MATERIAL BALANCE FLOW SHEET FOR TYPE A FGD PROCESS, 85% SO_2 STREAM, AIR-BLOWN GASIFIER


Dry Coal, 296.3 T/D
Air ①
Steam ②
Gasifier
Raw Gas ③
Water Air
④
Gas Cleanup and Reheat
Cleaned Gas ⑤
SO_2-Rich Stream from FGD
⑥
1st Stage Reducer
2nd Stage Reducer (Claus)
⑦
Air
⑧
Tail Gas Incinerator
Tail Gas Recycle to FGD
⑨
Bottom Ash
Fly ash, Tar, Water
Sulfur, 299.9 T/D

	lb mole/hr for 1000-MW Power Plant								
Specie	①	②	③	④	⑤	⑥	⑦	⑧	⑨
H_2			661.6		604.4		87.6		0.
CO			1260.5		1151.5		167.0		0.
CO_2			150.2		269.6	542.8	1796.9		2072.3
CH_4			118.7		108.4		108.4		0.
H_2S			26.8		22.6		3.3		0.
SO_2					2.0	798.3	40.0		43.3
N_2	2205.2		2205.2	471.8	2677.0	1373.1	4050.1	1401.7	5451.8
H_2O		548.3	496.5		656.1	479.0	1671.2		1978.9
O_2	586.2			125.4	11.4		11.4	372.6	35.0
Other			33.8		9.4		9.0		9.0
Total	2791.4	548.3	4953.3	597.2	5512.0	3193.2	7944.9	1774.3	9590.3
Temperature, C	27	121	177	27	343	27	288	27	
Temperature, F	80	250	350	80	650	80	550	80	

FIGURE 11-4. MATERIAL BALANCE FLOW SHEET FOR TYPE A FGD PROCESS, 25% SO_2 STREAM, AIR-BLOWN GASIFIER

TABLE 11-2. INVESTMENTS FOR REDUCTION OPTIONS, TYPE A FGD PROCESS, 1000-MW POWER PLANT

	Allied Process (Natural Gas)		Coal Gasification			
Inlet SO_2 Concentration (vol %)	85	25	85	85	25	25
Gasification Agent			O_2	Air	O_2	Air
1975 Investment[(a)] (10^3\$)						
Gasification system			8,110	8,372	8,110	8,372
Oxygen plant			5,180		5,180	
Claus plant			3,967	5,983	5,444	7,168
Ductwork			29	42	36	47
Blowers			52	113	65	128
Total	8,258	11,837	17,338	14,510	18,836	15,715
Total Investment in \$/kW	8.3	11.8	17.3	14.5	18.8	15.7
Mole % $H_2 + CO + H_2S + SO_2$ at first reduction stage			79.3	40.0	46.8	29.6

(a) Chemical Engineering Plant Cost Index = 190, Marshall & Stevens Equipment Cost Index = 460. Investments are based on flow rates 10 percent greater than those shown on material balance flow sheets.

TABLE 11-3. INVESTMENTS FOR REDUCTION OPTIONS, TYPE A FGD PROCESS, 500-MW POWER PLANT

	Allied Process (Natural Gas)		Coal Gasification			
Inlet SO_2 Concentration (vol %)	85	25	85	85	25	25
Gasification Agent			O_2	Air	O_2	Air
1975 Investment[(a)] (10^3\$)						
Gasification system			4,992	5,153	4,992	5,153
Oxygen plant			3,188		3,188	
Claus plant			2,617	3,947	3,592	4,729
Ductwork			21	30	26	34
Blowers			32	41	70	79
Total	6,062	8,587	10,850	9,171	11,868	9,995
Total Investment in \$/kW	12.1	17.2	21.7	18.3	23.7	20.0
Mole % $H_2 + CO + H_2S + SO_2$ at first reduction stage			79.3	40.0	46.8	29.6

(a) Chemical Engineering Plant Cost Index = 190, Marshall & Stevens Equipment Cost Index = 460. Investments are based on flow rates 10 percent greater than those shown on material balance flow sheets.

Systems based on oxygen-blown gasifiers require greater investments than those based on air-blown gasifiers. The cost of an air-blown gasification system is only slightly greater than that of an oxygen-blown system (excluding the oxygen plant), and this difference is due to a small increase in capacity because of a greater reheat requirement.* The greater gas volumes for an air-blown system increase the cost of the reduction system and other equipment, but this increase is not as great as the cost of the oxygen plant for the oxygen-blown system.

Operating Costs

The estimated operating costs for reduction systems for 1000-MW and 500-MW power plants are presented in Tables 11-4 and 11-5, respectively. The unit costs used in calculating these operating costs are shown in Table 11-6. For the coal-based cases, two coal costs are considered, \$10 and \$30 per ton, since there is currently a wide range of coal prices. Even with coal at \$10/ton the operating cost for the coal-based systems are consistently greater than those for the Allied process. Again, the air-blown systems are less costly than the oxygen-blown systems.

Comments

Although the costs for systems based on air-blown gasifiers are less than those for oxygen-blown gasifiers, the choice between these two is not obvious. In some cases, particularly for the more dilute SO_2 streams, the additional dilution caused by the use of air-blown gasifiers may decrease the reaction rates in the reduction system to a point where satisfactory sulfur recovery cannot be obtained. As the composite H_2S + SO_2 stream entering a Claus plant becomes more dilute, the efficiency of sulfur recovery decreases. This effect for a two-stage Claus plant is illustrated in Table 11-7. For a three-stage Claus plant the recoveries will be higher but the trend will be the same. Thus, for reduction of relatively dilute SO_2 streams, the gasification may have to be done with oxygen.

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* Reheating the reducing gas to 340 C (650 F) after the water wash increases the coal fed to the gasifier by about 8.7 percent for the air-blown case versus 4.5 percent for the oxygen-blown case. (See Appendix F.)

TABLE 11-4. OPERATING COSTS FOR REDUCTION OPTIONS, TYPE A FGD PROCESS, 1000-MW POWER PLANT
75 Percent Load Factor

	Allied Process (Natural Gas)		Coal Gasification			
Inlet SO_2 Concentration (vol %)	85	25	85	85	25	25
Gasification Agent			O_2	Air	O_2	Air
Operating Cost, 10^3\$/yr						
Natural gas	1,016	1,016				
Coal, \$10/T (\$30/T)			788 (2,364)	811 (2,433)	788 (2,364)	811 (2,433)
Electricity						
Gasification system			19	19	19	19
O_2 plant			249		249	
Reduction system	44	44	44	44	44	44
Blowers, etc.	14	19	18	27	20	20
Steam						
Gasification system			-129		-129	
Reduction system	-24	-18	-24	-24	-24	-24
Water						
Gasification system			37	39	37	39
O_2 plant			6	6	6	6
Reduction system	29	29	29	29	29	29
Catalysts & chemicals						
Gasification system			6	6	6	6
O_2 plant			59		59	
Reduction system	4	4	4	4	4	4
Total Feed and Utilities	1,083	1,094	1,106 (2,682)	961 (2,583)	1,108 (2,684)	964 (2,586)
Operating labor	237	237	377	259	377	259
Investment related (24%/yr)	1,982	2,841	4,161	3,482	4,521	3,772
Total Gross	3,302	4,172	5,644 (7,220)	4,702 (6,324)	6,006 (7,582)	4,995 (6,617)
Sulfur credit (\$10/LT)	-713	-713	-733	-733	-733	-733
Total Net	2,589	3,459	4,911 (6,487)	3,969 (5,591)	5,273 (6,849)	4,262 (5,884)
Net Operating Cost in mills/kWh	0.39	0.53	0.75 (0.99)	0.60 (0.85)	0.80 (1.04)	0.65 (0.90)
Net Operating Cost in \$/LT Sulfur	36	49	67 (89)	54 (76)	72 (93)	58 (80)

Note: \$/metric ton = 1.103 (\$/T) = 0.9844 (\$/LT).

TABLE 11-5. OPERATING COSTS FOR REDUCTION OPTIONS, TYPE A FGD PROCESS, 500-MW POWER PLANT

75 Percent Load Factor

	Allied Process (Natural Gas)		Coal Gasification			
Inlet SO_2 Concentration (vol %)	85	25	85	85	25	25
Gasification Agent			O_2	Air	O_2	Air
Operating Cost, 10^3 \$/yr						
Total feed and utilities[(a)]	542	547	553 (1,341)	481 (1,292)	554 (1,342)	482 (1,293)
Operating labor[(b)]	193	193	306	210	306	210
Investment related (24%/yr)	1,455	2,061	2,604	2,201	2,848	2,399
Total Gross	2,190	2,801	3,463 (4,251)	2,892 (3,703)	3,708 (4,496)	3,091 (3,902)
Sulfur credit (\$10/LT)	-357	-357	-366	-366	-366	-366
Total Net	1,833	2,444	3,097 (3,885)	2,526 (3,337)	3,342 (4,130)	2,725 (3,536)
Net Operating Cost in mills/kWh	0.56	0.74	0.94 (1.18)	0.77 (1.02)	1.02 (1.26)	0.83 (1.08)
Net Operating Cost in \$/LT Sulfur	51	69	85 (106)	69 (91)	91 (113)	74 (96)

(a) One-half of value for 1000-MW plant.

(b) Scaled down from 1000-MW case using 0.3 power of capacity.

Note: \$/metric ton = 1.103 (\$/T) = 0.9844 (\$/LT).

TABLE 11-6. UNIT COSTS USED IN OPERATING COST CALCULATIONS

Item	Cost
Natural gas	\$0.75/10^3 scf
Coal	\$10/ton (\$30/ton)
Electricity	\$0.012/kWh
Steam	\$0.50/10^6 Btu(a)
Process water	\$0.25/10^3 gal
Boiler feed water	\$0.50/10^3 gal
Operating labor	\$9/hour total cost

(a) Heat relative to saturated liquid water at 49 C (120 F).

Conversion factors:
\$/std m^3 = 35.31 (\$/scf)
\$/metric ton = 1.103 (\$/ton)
\$/10^6 kcal = 3.953 (\$/10^6 Btu)
\$/10^3 liter = 0.2642 (\$/10^3 gal)

TABLE 11-7. EFFECTS OF SO_2 DILUTION ON SULFUR RECOVERY IN TWO-STAGE CLAUS PLANT

Inlet $H_2S + SO_2$ Concentration, volume percent dry basis	Sulfur Recovery, percent
20	92.7
40	93.5
60	94.4
80	95.0

Source: Kim, B. C., et al (Reference 30).

The operating cost calculations for the oxygen-blown systems include a rather substantial credit for steam produced in the gasification system. Since the oxygen-blown cases are based on the Koppers-Totzek gasifier, data on the steam production by K-T gasifiers were used. Using the data for Illinois coal (Table C-1) plus two material balances obtained from Koppers,(31,32) the net steam productions and heat contents thereof were calculated. The average net steam production for these cases was 1,436 kg/metric ton dry coal (2,990 lb/ton) or 0.912×10^6 kcal/metric ton dry coal (3.27×10^6 Btu/ton) of energy relative to liquid water at 49 C (120 F). This is primarily high temperature (e.g., 260 C or 500 F) steam which can be used in the FGD process or the boiler itself. No steam credit was taken for the air-blown cases, since the available data on Wellman-Galusha systems showed neither a steam credit nor a cost. Air-blown gasifiers generally operate at lower temperatures than oxygen-blown gasifiers and hence generate less steam and lower temperature steam. It is probably reasonable to assume that the steam generated by such a gasifier will just meet its own steam requirement.

Although comparisons of the coal-based reduction systems with the Allied process are instructive, it should be kept in mind that these two options accomplish a rather different objective because of the difference in the starting materials. The use of a "dirty" (sulfur-containing) reductant would be expected to cost more than the use of a clean reductant (natural gas), just as the use of dirty fuels in an environmentally sound manner generally costs more than the use of clean fuels. The present and projected shortage of natural gas will require factors other than cost to be considered.

The general level of the reduction costs are worth noting. For a 1000-MW power plant fired with 3.5 percent sulfur coal, any type of SO_2 reduction system will add 8-19 $/kW to the investment for the power plant and 0.4-1.0 mills/kWh to the operating cost. This represents a significant fraction, roughly 15 percent, of the estimated cost of the FGD process itself. The costs reflect the fact that the reduction step further decreases the overall energy conversion efficiency of the power plant. The increase in the complexity of the power plant is apparent from the flow sheets presented in this section. This is not meant to imply that the reduction step is undesirable, since it is a necessary part of a sulfur-producing FGD system. It is important to recognize all the costs and other disadvantages which are concomitant with the advantages of an FGD system which is environmentally acceptable in all respects.

11.2 Type B FGD Processes

The Type B FGD processes require H_2S as a reductant because these processes include liquid-phase Claus reactors. The reduction of some of the elemental sulfur to generate the H_2S can be done with commercially available processes such as the Thio-Pet and Girdler processes. It is possible that a coal-based H_2/CO mixture could be used directly in a process of this type in place of the H_2-rich gases which have been used to date. Thio-Pet personnel are optimistic about this on the basis of some thermodynamic calculations they have made (these were discussed in Section 9). However, they are quick to point out that this has not been tested experimentally.

Lacking a demonstration of this more direct route, it seemed advisable to estimate the costs associated with the conventional technology, i.e., using a H_2-rich stream for the H_2S generation. Hydrogen sulfide generation plants operating today use a reductant gas containing at least 80 percent H_2. Producing such a gas from coal gas requires an oxygen-blown gasifier plus two stages of CO shifting and acid gas removal. A flow sheet for a coal-based H_2S generation system is shown in Figure 11-5, and the associated stream compositions and flow rates are given in Table 11-8.

Investments

The investments for coal-based H_2S generation systems for use with Type B FGD processes are shown in Table 11-9. The investment for the H_2S generation facility itself is a quotation supplied by C & I/ Girdler, Inc.,(33) for this project. The investment for the reductant gas upgrading equipment (shift converters, acid gas removal facilities,

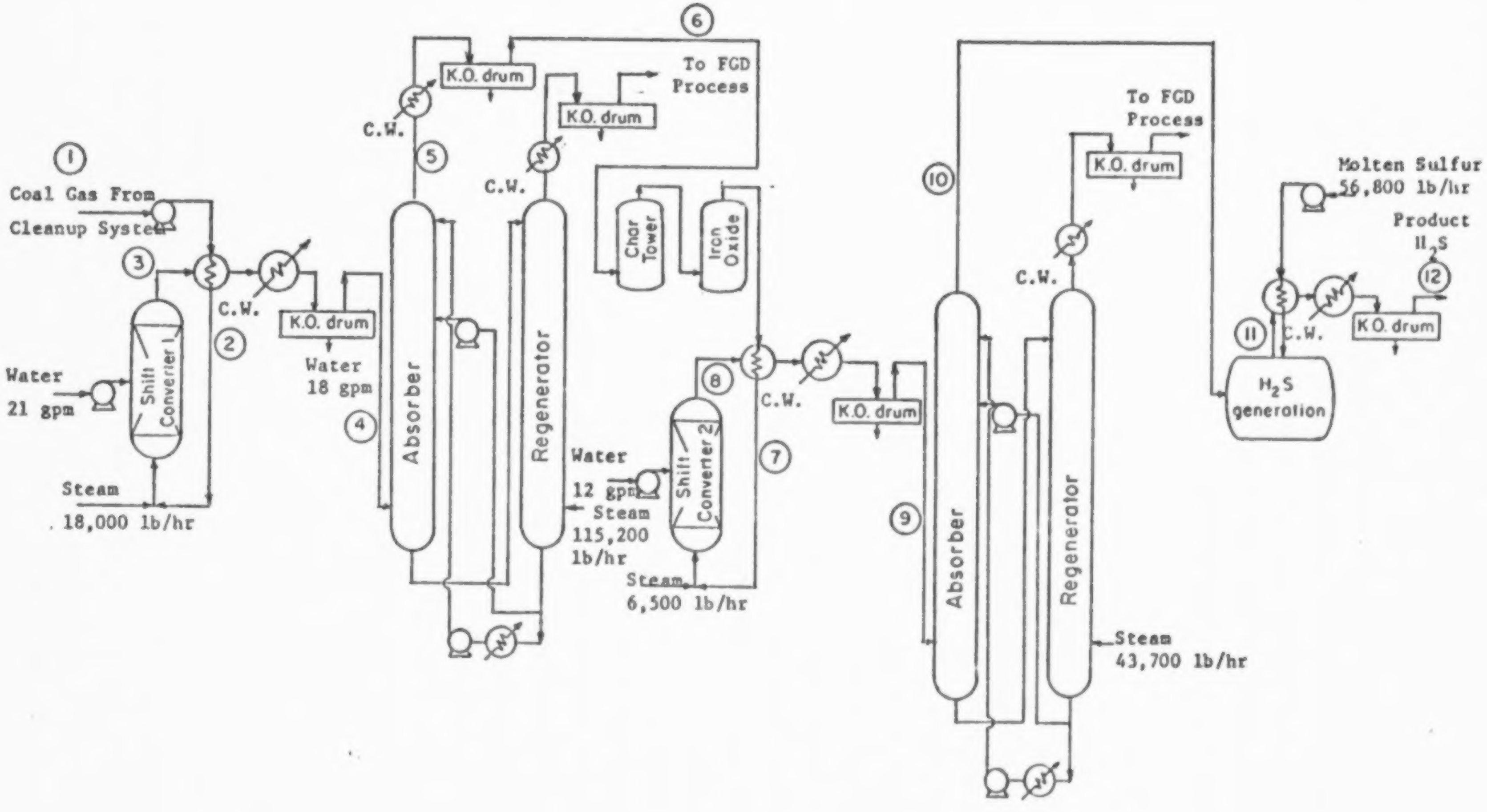
①
Coal Gas From
Cleanup System
③
②
C.W.
Water
21 gpm
Shift Converter 1
Steam
18,000 lb/hr
K.O. drum
Water
18 gpm
④
C.W.
⑤
K.O. drum
Absorber
Regenerator
C.W.
K.O. drum
⑥
To FGD
Process
Char Tower
Iron Oxide
Water
12 gpm
Steam
115,200
lb/hr
Shift Converter 2
⑧
Steam
6,500 lb/hr
C.W.
⑦
K.O. drum
⑨
⑩
Absorber
Regenerator
C.W.
K.O. drum
To FGD
Process
Steam
43,700 lb/hr
H₂S
generation
⑪
C.W.
Molten Sulfur
56,800 lb/hr
Product
H₂S
⑫
K.O. drum

FIGURE 11-5. MATERIAL BALANCE FLOW SHEET FOR H_2S PRODUCTION BASED ON COAL GASIFICATION

TABLE 11-8. COMPOSITIONS AND FLOW RATES FOR H_2S PRODUCTION BASED ON COAL GASIFICATION

Stream Number[(a)]	1	2	3	4	5	6	7	8	9	10	11	12
Temperature, C	52	316	482	107	110	38	204	260	107	110	454	54
Temperature, F	125	600	900	225	230	100	400	500	225	230	850	130
Pressure, psia	15	120	120	120	120	120	120	120	120	120	120	15
Composition, mole percent												
H_2	30.65	30.65	39.11	44.89	72.76	76.76	76.76	67.59	67.59	90.50	1.56	1.81
CO	49.06	49.06	8.15	9.35	15.15	15.99	15.99	1.43	1.43	1.91	0.33	0.38
CO_2	6.24	6.24	24.64	28.28	4.59	4.84	4.84	14.07	14.07	1.89	1.63	1.81
CH_4	0.10	0.10	0.06	0.07	0.11	0.12	0.12	0.09	0.09	0.12	0.04	0.05
H_2S	1.04	1.04	0.62	0.71	--	--	--	--	--	--	76.71	88.70
COS	0.10	0.10	0.06	0.07	--	--	--	--	--	--	1.32	1.53
N_2	0.89	0.89	0.53	0.61	0.98	1.04	1.04	0.77	0.77	1.03	0.89	1.03
Ar	0.40	0.40	0.24	0.27	0.44	0.47	0.47	0.35	0.35	0.46	0.40	0.46
CS_2	--	--	--	--	--	--	--	--	--	--	0.06	0.07
S	--	--	--	--	--	--	--	--	--	--	13.51	--
H_2O	11.52	11.52	26.61	15.76	5.97	0.79	0.79	15.71	15.71	4.08	3.53	4.08
Total	100.00	100.00	100.02	100.01	100.00	100.01	100.01	100.01	100.01	99.99	99.98	100.00
Total Flow Rate												
10^3 lb-moles/hr	2.319	2.319	3.912	3.408	2.103	1.993	1.993	2.678	2.678	2.000	2.313	2.000
10^6 ft^3/hr	0.969	0.219	0.475	0.208	0.130	0.100	0.153	0.230	0.164	0.123	0.270	0.843

(a) Refer to Figure 13-5.

Conversion factors: kg/m^2 abs. = 703.1 (psia), g-moles/hr = 453.6 (lb-moles/hr), m^3/hr = 0.02832 (ft^3/hr).

TABLE 11-9. INVESTMENT FOR H_2S GENERATION SYSTEM FOR TYPE B FGD PROCESS

Power Plant Capacity	1000 MW	500 MW
1975 Investment (10^3\$)		
Gasification system	8,141	5,011
Oxygen plant	4,840	2,979
Shift converter 1	295	182
Waste heat recovery system	1,885	1,160
Acid gas removal 1[a]	5,047	2,524
Shift converter 2	466	287
Acid gas removal 2	1,773	1,091
H_2S generation facility[b]	9,700	4,850
Total	32,147	18,084
Total Investment in $/kW	32.1	36.1

(a) Two trains for 1000 MW, one train for 500 MW.

(b) Four trains for 1000 MW, two trains for 500 MW.

etc.) are based on cost data obtained from the Bureau of Mines$^{(34)}$ on making hydrogen from coal gas. Adjustments were made for capacity and operating pressure.

The investments shown in Table 11-9 are 1.5-2.2 times greater than the investments for coal-based reductant systems for Type A FGD processes (Tables 11-2 and 11-3). The investment would be reduced by about 7 percent if the second stage of shifting and acid gas removal could be eliminated and by about 30 percent if both stages could be eliminated.

Operating Costs

The operating costs for the coal-based H_2S generation systems are shown in Table 11-10. The requirements of the H_2S generation facility itself were supplied by Girdler. The steam requirement for the reductant upgrading steps, which is quite large, was determined by material and energy balances.

The total operating costs shown in Table 11-10 are 1.5-2.5 times greater than the operating costs for coal-based reductant systems for Type A FGD processes (Tables 11-4 and 11-5). The total cost of H_2S made in this manner is \$55-\$71/metric ton (2.5-3.2¢/lb), depending on the coal price and plant size. An "across the fence" purchase of H_2S for use as a reductant (the concept discussed in Section 6) would be economical only if the prices were lower than these cost levels as applied to the specific situation. Only by-product H_2S streams could meet this requirement; high purity merchant H_2S would be expensive.

Comment

It should be noted that a portion of the costs shown here would be incurred even if the H_2S were to be made from natural gas instead of coal. In this case, the cost of the H_2S generation facility itself would be the same as shown here, the cost of the gas upgrading step would be somewhat lower (less CO shifting and CO_2 removal), and the cost of a steam reforming plant for the natural gas would be less than that of the coal gasification system.

TABLE 11-10. OPERATING COSTS FOR H_2S GENERATION SYSTEM FOR TYPE B FGD PROCESS

Power Plant Capacity	1000 MW	500 MW
Operating Cost (10^3\$/yr)		
Coal, \$10/T (\$30/T)	792 (2,377)	
Electricity		
Gasification system	19	
O_2 plant	231	
H_2S generation facility	36	
Other	22	
Steam		
Gasification system	-130	
Shift converters, regenerators	648	
H_2S generation facility	76	
Water		
Gasification system	37	
O_2 plant	6	
H_2S generation facility	14	
Other	10	
Catalysts & chemicals		
Gasification system	6	
O_2 plant	54	
Other	10	
Total Feed and Utilities	1,831 (3,416)	916 (1,708)
Operating labor	377	306
Investment related (25%/yr)	7,715	4,340
Total	9,923 (11,508)	5,562 (6,354)
Operating Cost in mills/kW	1.51 (1.75)	1.69 (1.93)
Operating Cost in \$/metric ton H_2S	55.1 (63.9)	61.7 (70.6)

Note: Elemental sulfur for H_2S generation facility is taken as having no cost.

11.3 Other Considerations

There is one aspect of the integration of a coal gasification-based reduction system with an FGD process to which an allusion was made earlier in this section which warrants further discussion. This involves the fact that the gasification system, in addition to supplying the reductant, can supply at least part of the energy requirements of the FGD process. For the wet FGD processes, the major use of energy is for reheating the cleaned flue gas. The energy requirement for reheating the flue gas is about 0.15×10^6 kcal/metric ton (0.52×10^6 Btu/ton) of coal fired to the boiler (see Appendix F). As mentioned previously, a Koppers-Totzek gasifier produces about 0.912×10^6 kcal/metric ton of coal gasified in usable heat as high temperature steam. Since the quantity of coal fed to the gasifier is about 3.6 percent of that fed to the boiler, the heat available from the by-product steam is

$(0.036)(0.912 \times 10^6) = 0.033 \times 10^6$ kcal/metric ton of coal fired to boiler.

Thus, with a Koppers-Totzek gasifier about one-fourth of the reheat requirement could be met with the by-product steam. For other gasifiers operating at lower temperatures and hence producing less steam, a lower fraction of the reheat requirement could be met in this way. Even though the by-product steam can only partially satisfy the reheat requirement, the quantity of heat is large and the economic credit for it is substantial.

Additional energy, beyond that available from by-product steam, can be supplied to the FGD process for some uses by increasing the size of the gasification system and using the low- or intermediate-energy fuel gas directly. The flue gas can be reheated by burning some fuel gas and mixing the combustion products with the flue gas. Admittedly this adds some SO_2 to the cleaned flue gas, but this may be permissible if the SO_2 removal by the FGD process itself is high enough. The effect is similar to the option of reheating cleaned flue gas by bypassing some of the flue gas untreated.

11.4 Use of Oil Gasification

In order to investigate the effects of using residual oil as the gasification feedstock instead of coal, the Shell gasification process (SGP) for oil was compared with the coal gasification systems. The SGP is a partial oxidation process and includes facilities for removing the soot from the gas and recycling it to the gasifier. Therefore, it is comparable to a coal gasification system including the gas washing step.

This cost comparison is shown in Table 11-11. The coal gasification costs are from Tables 11-2 and 11-4. For the Shell process the investments and operating requirements (except labor) were taken from a paper by J. B. Plummer, et al, of Shell.(35) The operating labor was taken as the same as for coal gasification. It should be pointed out that the investments for the Shell process are subject to considerable error since they had to be scaled down from data for plants about 10 times as large. This scaling was done using a 0.7 exponent.

Compared to coal gasification, the investments for the Shell residual oil process are lower if oxygen is used for the gasification but slightly higher if air is used. One reason for the large difference in gasification system cost between the air- and oxygen-blown versions of the Shell process is that this is a high pressure process and hence the air-blown version requires extensive air compression facilities.

The price of residual oil is, like other energy costs, quite variable at this time. Therefore, two cost levels differing by a factor of three were used, just as was done for the coal. These costs were $5 and $15 per barrel. At these feedstock costs the total operating costs of the two processes are quite comparable if the gasification is done with oxygen. If the gasification is done with air, the Shell process is somewhat more expensive. The Shell process does deliver the reducing gas at an elevated pressure which could be an advantage for some particular applications. Of course, there are also high pressure coal gasification processes.

The choice between coal and oil as a feedstock for making reducing gas will depend largely on relative availability and convenience. In most cases this will mean that the power plant should produce reducing gas from the same fuel that it is using to fire its boilers.

TABLE 11-11. COST COMPARISON FOR COAL AND OIL GASIFICATION SYSTEMS

1000-MW Power Plant, 75 Percent Load Factor, Type A FGD Process

Gasifier Feed		Coal		Residual Oil	
Gasification Agent		O_2	Air	O_2	Air
1975 Investment (10^3\$)					
Gasification system		8,110	8,372	3,933	8,820
Oxygen plant		5,180		5,180[a]	
Total		13,290	8,372	9,113	8,820
Operating Cost (10^3\$/yr)					
Item	Unit Cost				
Coal	\$10/T (\$30/T)	788 (2,364)	811 (2,433)		
Residual oil	\$5/B (\$15/B)			1,321 (3,964)	1,388 (4,164)
Naphtha	\$12/B			32	32
Electricity	\$0.012/kWh	19	19	44	33
Steam	\$0.50/10^6 Btu	-129		55	-39
Water & chemicals		43	45	26	42
Operating labor	\$9/hr	377	259	377[a]	259[a]
Subtotal		1,098 (2,674)	1,134 (2,756)	1,855 (4,498)	1,715 (4,491)
Investment related (24%/yr)		3,190	2,009	2,187	2,117
Total		4,288 (5,864)	3,143 (4,765)	4,042 (6,685)	3,832 (6,608)
Operating Cost in mills/kWh		0.65 (0.89)	0.48 (0.73)	0.62 (1.02)	0.58 (1.01)

(a) Value taken to be same as for coal gasification.

12. CONCLUSIONS

The following conclusions, arranged by topics, may be drawn from the work discussed in this report.

Trace Constituents in Coal Based Reducing Gases

- Experimental data from the direct analysis of trace species in coal gases are not available, at least so far as public information is concerned. In the absence of such data, one can use either thermodynamically calculated concentrations or concentrations obtained by difference using coal and ash analyses.
- The general level of trace species in raw coal gas depends primarily on the composition of the specific coal and on the gasification temperature, with more species being present at higher temperatures.
- Removing particulate matter from the coal gas and the cooling necessarily associated with this operation will remove the great majority of the trace species from the gas. Water scrubbing will reduce the gas temperature to such an extent that only very low concentrations of trace species will remain in the gas. Scrubbing decreases the thermal efficiency of the system, thereby increasing the size of the gasifier.

Effects of Trace Constituents

- The effects of trace species in the coal-based reductant gas upon the FGD SO_2-removal step should be inconsequential, particularly if the gas is water scrubbed. Even without scrubbing, the quantities of coal involved indicate that the reductant gas would add less than 4 percent to the quantity of trace species already entering the FGD process via the flue gas.
- For the FGD processes which produce a concentrated SO_2 stream, the process will be followed by an SO_2 reduction reactor (e.g., the ASARCO type) and a vapor-phase Claus reactor. The only known adverse effect of trace species on these systems is that NH_3 will poison the Claus catalyst. Hence, the reducing gas must be water scrubbed.

- For the FGD processes which use a liquid-phase Claus reactor, H_2S must be generated from the reducing gas and sulfur. No catalyst is used in the liquid-phase Claus reactors, so no poisoning problems are possible. The only known adverse effect of trace species in this system is a side reaction caused by high COS concentrations. The COS can be hydrolyzed to H_2S, and in fact this may occur in the shift reactor which will precede the H_2S generator in at least some possible versions of this system.

Costs of Reductant Systems

- Reduction systems based on gasification of coal or residual oil will be relatively expensive, at least in comparison to systems based on natural gas. For an FGD process that produces a concentrated SO_2 stream, the cost of a gasification-based reduction system will be at least 15 percent of the estimated cost of the FGD process itself. For an FGD process that requires H_2S, this figure will be close to 30 percent unless technology can be developed for using the reducing gas without shifting or acid gas removal.

Complexity and Side Benefits

- A gasifier-based reduction system will significantly increase the complexity of the overall FGD system. On the other hand, there are other possible benefits of such a reduction system. The gasifier could be used to supply some of the energy requirements of the FGD process, such as for stack gas reheating. This energy could be supplied either as excess by-product steam from the gasifier or as excess fuel gas produced.

Use of Purchased H_2S as Reductant

- Purchased hydrogen sulfide will play only a minor role as a reductant for SO_2 from power plant FGD systems. The use of purchased H_2S will involve almost entirely by-product streams obtained "across the fence" from a source such as an oil refinery or a natural gas processing plant, and hence geographical considerations will restrict this usage.

13. RECOMMENDATIONS

Based on the work reported here, recommendations are made for experimental studies in three areas, which are described below.

1. Trace Species in Coal Gases

Experimental measurements of the concentrations of trace species in raw and water washed gases from leading coal gasification processes should be made.

Probably the most meaningful way to do this would be to sample streams from one of the commercial Koppers-Totzek gasifiers operating overseas. Since this is the highest temperature gasifier now available, it has the greatest potential for transferring trace species from the coal into the gas.

2. Use of Coal Gas as SO_2 Reductant

The use of coal gas as a reductant in the ASARCO SO_2 reduction system should be studied. The objectives would be to determine whether shifting of CO to H_2 is required and whether trace species in the water washed gas have any detrimental effects on the catalysts. Depending on these results, it may also be desirable to study the effects on a cobalt-molybdenum catalyst (the alternative for the first reduction stage).

It is our understanding that ASARCO is now conducting some studies in this area using their catalyst and presumably their pilot plant. Although this should be a valuable start, small-scale experiments are limited in that they cannot normally use real coal gas but only blends which simulate it. Therefore, tests on a demonstration-scale (>100-megawatt) FGD system should be conducted as soon as this is feasible. The NIPSCO unit of the Wellman-Lord process, which will be started up soon, would be a good facility for such testing. The NIPSCO unit includes the Allied Chemical SO_2 reduction process (using natural gas).

3. Use of Coal Gas in H_2S Generation

The use of coal gas to provide a reductant for elemental sulfur in an H_2S generation process, such as the Girdler or Thio-Pet processes, should be studied. The objective would be to define the minimum amount of processing (shift conversion, acid gas removal, etc.) of the coal gas required for satisfactory operation of the H_2S generation facility. The use of H_2S generated from coal gas in an FGD process such as the Citrate process which contains a liquid-phase Claus reactor should be studied.

The limitations of small-scale tests previously mentioned apply as well to this research area. However, there are as yet no demonstration-scale units for FGD processes of the type involved here. Such a unit for the Citrate (or Citrex) process may be built in the near future. In the meantime, some work in this area could be started using one of the two existing Citrate pilot plants. The USBM pilot plant in Kellogg, Idaho, has the advantages that it includes the Thio-Pet H_2S generation process (using natural gas) and is currently in operation. However, this plant treats smelter gas rather than power plant flue gas. The Peabody Citrex pilot plant in Terre Haute, Indiana, has the advantage that it treats flue gas from a coal-fired boiler. This plant is not presently in operation but could be restarted. It does not include an H_2S generation step (cylinder H_2S was used).

Work in the above areas will focus on the major technical uncertainties associated with the alternative principally addressed in this work, i.e., the gasification of a "dirty" (sulfur-containing) fuel to provide a reducing gas for use with FGD systems. There are alternatives which accomplish the same objective and which were discussed only briefly in this report. One is Foster-Wheeler's RESOX process, which reduces SO_2 directly with coal. Another is the Atomics International Aqueous Carbonate FGD process, which accomplishes its regeneration directly with coke or coal. Research on these alternatives should also be continued until the relative advantages of the various options are clarified and the field can be narrowed.

14. ACKNOWLEDGMENTS

A number of individuals and organizations contributed their advice and assistance to this study. In this regard, the Project Officers for these tasks, Dr. Charles Chatlynne and Mr. Roger C. Christman,* as well as Mr. Richard D. Stern of EPA deserve mention. The Allied Chemical Company and the Electric Power Research Institute provided a number of helpful suggestions after reviewing draft reports on this project. Several staff members of Battelle-Columbus also contributed to this study, including G. R. Smithson, Jr., E. H. Hall, P. S. K. Choi, and D. A. Ball. T. W. Zegers and D. M. Jenkins contributed to the study of the use of purchased hydrogen sulfide. D. M. Treweek, a consultant to Battelle-Columbus, contributed to the thermodynamic predictions of trace constituent distributions.

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* Mr. Christman served as Project Officer for most of the work done on these tasks.

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APPENDIX A

FLUE GAS DESULFURIZATION PROCESSES

APPENDIX A

FLUE GAS DESULFURIZATION PROCESSES

This appendix presents some additional information on flue gas desulfurization processes in general and on the analysis which was made of the reduction requirements of some of these processes.

Classification of Processes by Type of Operation

There are two general types of flue gas desulfurization processes - the "throwaway" processes which produce an unusable mixture of sulfur compounds and the "regenerable" processes which produce saleable by products. The throwaway processes, particularly lime and limestone scrubbing, are generally at a more advanced stage of development than the regenerable processes. Only the regenerable processes are of interest in this study.

Figure A-1 shows a functional classification of the regenerable flue gas desulfurization processes. The three types of processes of interest in this study are those using absorption by liquids, sorption by solids, and catalytic reduction. Typical processes currently under development in these three groups are shown in Figures A-2, A-3, and A-4.

Detail on Reduction Requirements of Sulfur-Producing Processes

A classification of sulfur-producing FGD processes according to their reduction requirements was presented in Section 3 of the text. For the Type A processes, which produce concentrated SO_2 streams, typical SO_2 concentrations in the product streams were given (Table 3-1) and average compositions were developed for each of the two classes of Type A processes. As backup information, brief process descriptions are given in this section with emphasis on where the stream requiring reduction comes from and what it contains.

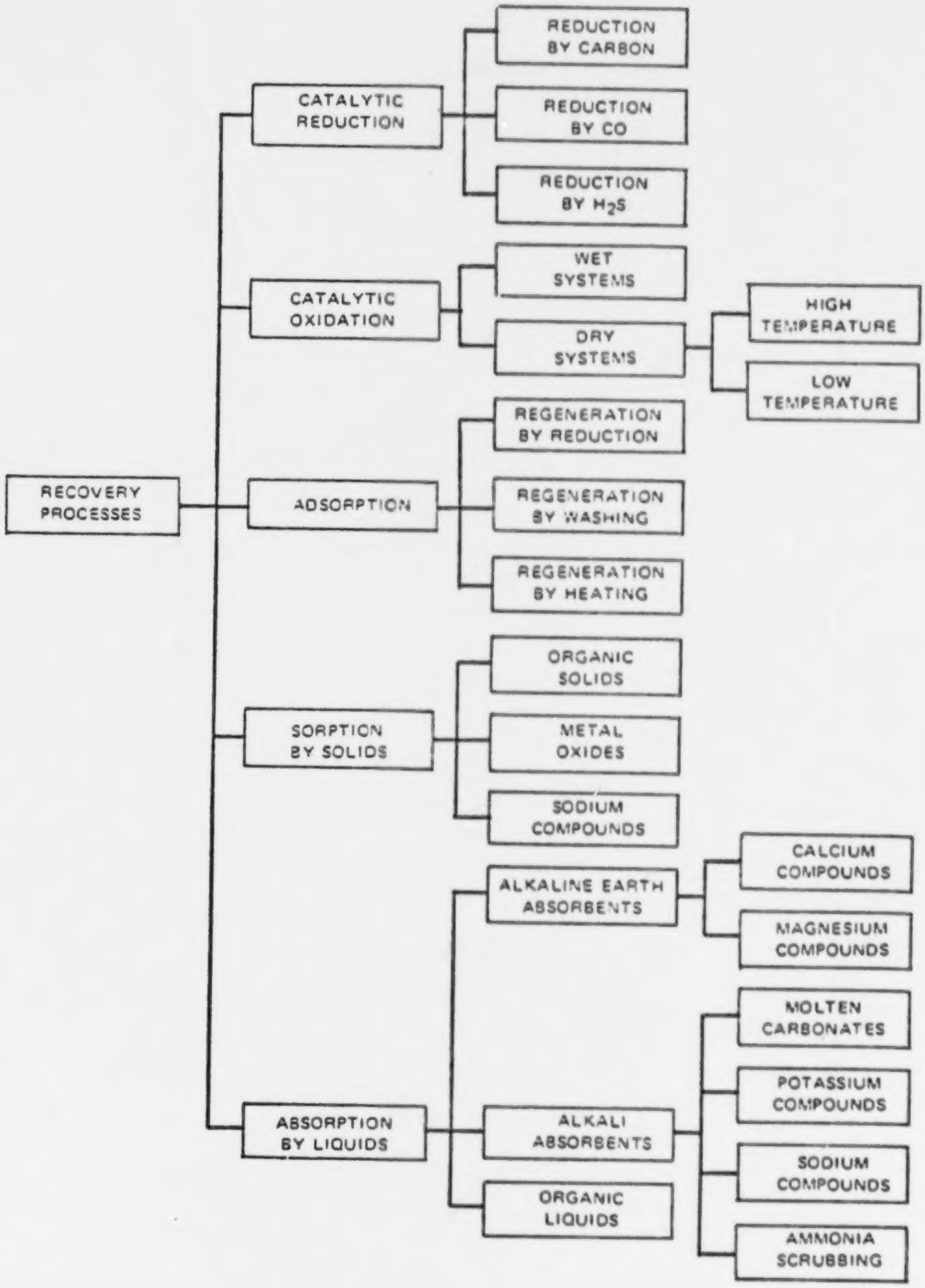
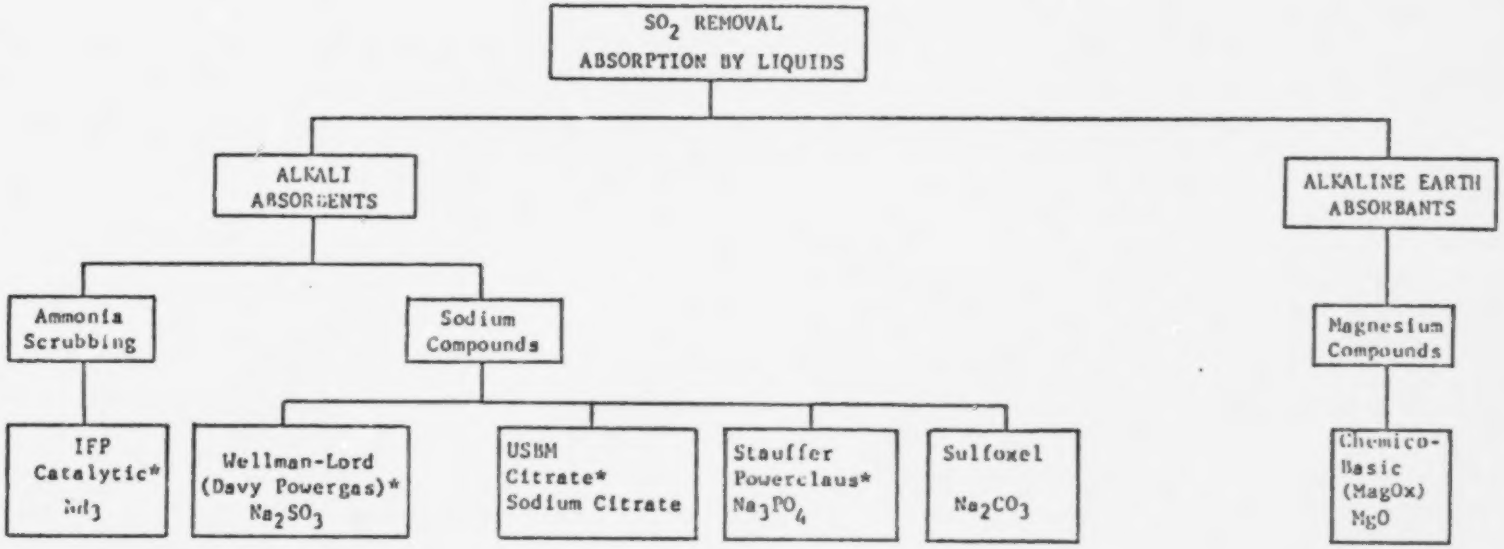
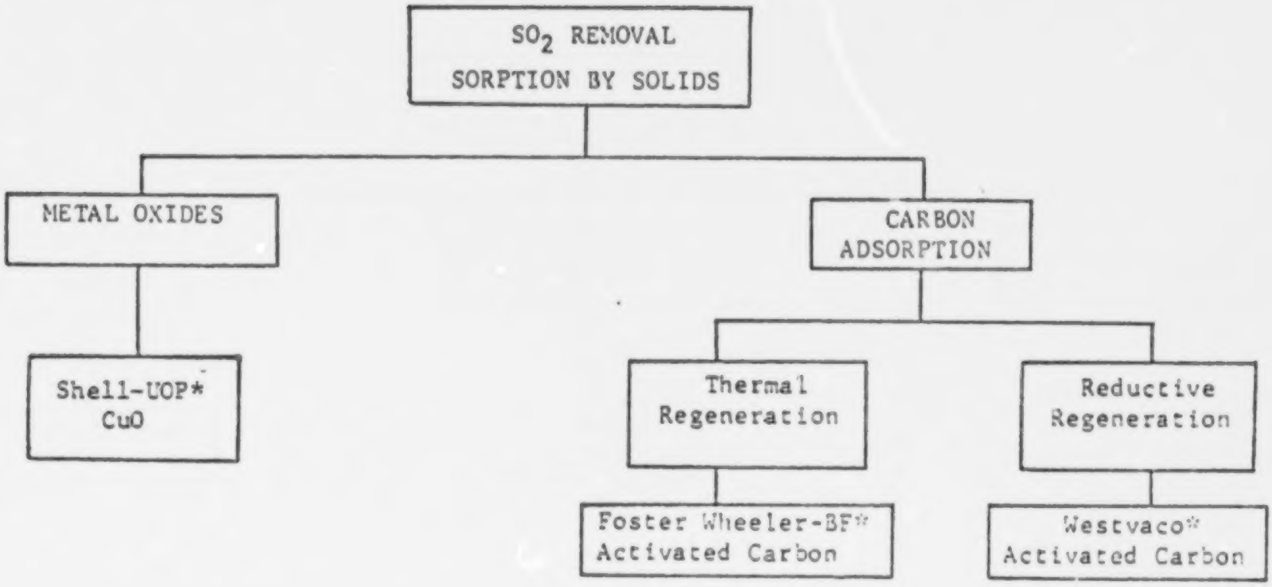

RECOVERY PROCESSES
CATALYTIC REDUCTION
REDUCTION BY CARBON
REDUCTION BY CO
REDUCTION BY H_2S
CATALYTIC OXIDATION
WET SYSTEMS
DRY SYSTEMS
HIGH TEMPERATURE
LOW TEMPERATURE
ADSORPTION
REGENERATION BY REDUCTION
REGENERATION BY WASHING
REGENERATION BY HEATING
SORPTION BY SOLIDS
ORGANIC SOLIDS
METAL OXIDES
SODIUM COMPOUNDS
ABSORPTION BY LIQUIDS
ALKALINE EARTH ABSORBENTS
CALCIUM COMPOUNDS
MAGNESIUM COMPOUNDS
ALKALI ABSORBENTS
MOLTEN CARBONATES
POTASSIUM COMPOUNDS
SODIUM COMPOUNDS
AMMONIA SCRUBBING
ORGANIC LIQUIDS

FIGURE A-1. SELECTED TECHNOLOGIES FOR THE REMOVAL OF SO_2 FROM STACK GAS


SO_2 REMOVAL
ABSORPTION BY LIQUIDS
ALKALI ABSORBENTS
ALKALINE EARTH ABSORBANTS
Ammonia Scrubbing
Sodium Compounds
Magnesium Compounds
IFP Catalytic* NH_3
Wellman-Lord (Davy Powergas)* Na_2SO_3
USBM Citrate* Sodium Citrate
Stauffer Powerclaus* Na_3PO_4
Sulfoxel Na_2CO_3
Chemico-Basic (MagOx) MgO

*Example only--other similar processes exist

FIGURE A-2. SELECTED TECHNOLOGIES FOR THE REMOVAL OF SO_2 FROM STACK GAS BY LIQUID ABSORPTION


SO_2 REMOVAL
SORPTION BY SOLIDS
METAL OXIDES
CARBON ADSORPTION
Shell-UOP* CuO
Thermal Regeneration
Reductive Regeneration
Foster Wheeler-BF* Activated Carbon
Westvaco* Activated Carbon

*Example only--other similar processes exist.

FIGURE A-3. SELECTED TECHNOLOGIES FOR THE REMOVAL OF SO_2 FROM STACK GAS BY SOLIDS SORPTION

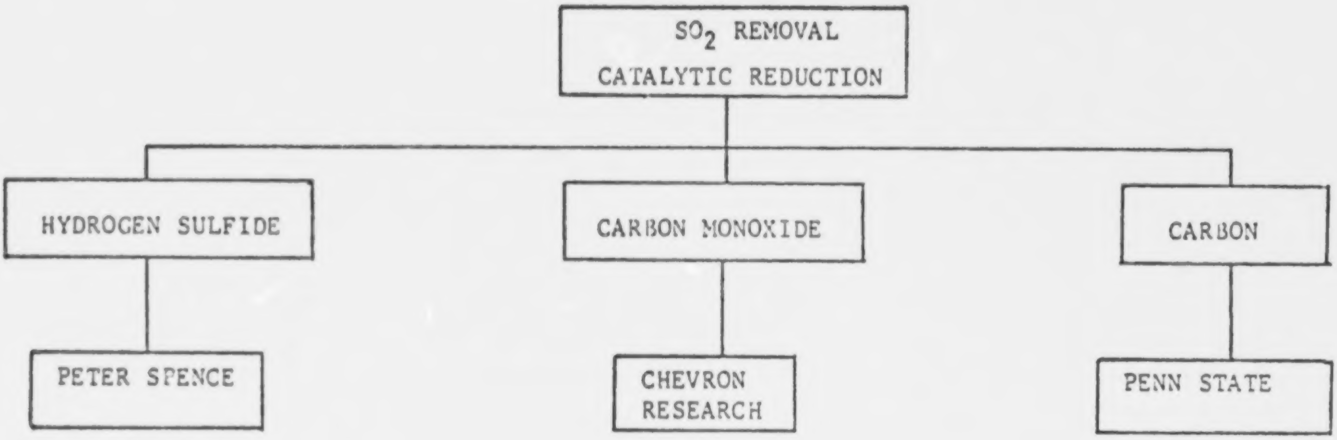

SO_2 REMOVAL
CATALYTIC REDUCTION
HYDROGEN SULFIDE
CARBON MONOXIDE
CARBON
PETER SPENCE
CHEVRON RESEARCH
PENN STATE

FIGURE A-4. SELECTED TECHNOLOGIES FOR THE REMOVAL OF SO_2 FROM STACK GAS BY CATALYTIC REDUCTION

Wellman-Lord (Davy Powergas)

General Description. The SO_2 is absorbed by a solution of sodium sulfite, thereby forming sodium bisulfite. The solution is thermally regenerated in a crystallizer, liberating SO_2.

Product Stream. The gas from the crystallizer contains about 85 percent SO_2 with the balance being mostly water vapor.

Shell-UOP CuO

General Description. The SO_2 is picked up by reaction with a solid sorbent composed of copper on alumina, thereby forming $CuSO_4$. The sorbent beds are periodically regenerated with a hydrogen-steam mixture, liberating SO_2. The regeneration off-gas is concentrated in a quench tower and an absorber/stripper system.

Product Stream. The SO_2 concentration in the product stream is about 6 percent leaving the reactor, about 46 percent after the quench tower, and about 90 percent after the absorber/stripper. After the absorber/stripper, the stream contains only SO_2 and H_2O, but before this it also contains impurities from the hydrogen used for regeneration.

Special Reduction Requirements. A reductant is needed for two steps in this process: (1) for regenerating the sorbent and (2) for reducing the SO_2. For the former, Shell now feels that hydrogen must be used, although they have done some work on other reductants.

Ammonia Scrubbing

General Description. The SO_2 is absorbed by an aqueous ammonia liquor containing sulfite, bisulfite, and sulfate. The sulfites are thermally decomposed and the sulfates are reduced with recycled sulfur product, thereby producing an SO_2-rich gas. In one particular process, the IFP-Catalytic process, H_2S is generated by reducing SO_2 with an H_2-CO mixture and this H_2S is used to reduce the SO_2 to S in a liquid phase catalytic Claus reaction.

Product Stream. The SO_2-rich gas produced in the regeneration step contains about 27 percent SO_2, 24 percent H_2O, and 49 percent NH_3. After the SO_2 has been removed by reduction, the ammonia in this stream is recycled to the absorber.

Magnesia Scrubbing

General Description. The SO_2 is absorbed by an aqueous slurry of MgO, thereby forming hydrated $MgSO_3$ and $MgSO_4$. These salts are then dried to remove surface water and water of hydration and then decomposed in a calciner to form MgO and SO_2. The decomposition is thermal for the $MgSO_3$, but coke is added to reduce the $MgSO_4$.

Product Stream. Because the calciner is direct-fired (normally with oil), the product gas stream contains combustion gases. When the desired product is H_2SO_4, excess air is fed to the calciner to avoid contamination of the acid with sulfur. In this case, the gas contains about 24 percent SO_2, 56 percent N_2, 9 percent CO_2, 7 percent H_2O, and 4 percent O_2. When the desired product is sulfur, the excess air will evidently be reduced or eliminated. When this is done, carbon from the oil may serve to reduce some of the $MgSO_4$, thereby decreasing the need for coke.

Foster Wheeler-BF Carbon Adsorption

General Description. The SO_2 is adsorbed onto activated carbon in the form of H_2SO_4. A thermal regeneration at about 650 C (1200 F) decomposes the H_2SO_4, thereby liberating the SO_2.

Product Stream. Because the regeneration temperature is so high, oxygen in the system results in combustion of some of the carbon to form CO_2. The oxygen comes from two sources--air initially present (adsorbed on the carbon) and O_2 evolved from decomposition of the H_2SO_4. The product gas also contains N_2 from the initial air and H_2O from the decomposition of the H_2SO_4. The gas composition is about 23 percent SO_2, 33 percent N_2, 21 percent CO_2, and 23 percent H_2O.

U.S.B.M. Citrate

General Description. The flue gas is cooled and washed in a spray tower and then scrubbed with an aqueous solution of sodium citrate, citric acid, and sodium thiosulfate. These compounds buffer the solution, thereby increasing the absorption capacity, and inhibit oxidation of the sulfite to sulfate. The resulting solution, which contains about 10 g SO_2/liter, is contacted with H_2S in a stirred reactor, thereby reducing the SO_2 to sulfur. The sulfur is separated by oil or froth flotation and melting, and the citrate solution is recycled to the absorber. The H_2S is normally generated by reducing sulfur, in which case 2/3 of the total sulfur produced is recycled in this manner.

Stauffer Powerclaus

General Description.-The flue gas is cooled and washed in a spray tower and then scrubbed with an aqueous solution of Na_3PO_4. The resulting solution is contacted with H_2S in a stirred reactor, thereby reducing the SO_2 to sulfur. The sulfur is recovered by one of several available methods and is purified by autoclaving.

Westvaco Carbon Adsorption

General Description. The SO_2 is adsorbed onto activated carbon in the form of H_2SO_4. The H_2SO_4 is reduced to sulfur with H_2S, and the sulfur is stripped from the carbon with steam. Both the adsorption and the reduction steps are conducted in fluidized beds. The H_2S is normally generated by reducing sulfur with H_2 in a third fluidized bed. When this is done, only 1/4 of the total sulfur produced is stripped from the carbon, and the remainder is converted to H_2S while still on the carbon.

Aqueous Carbonate Process

General Description. The flue gas is scrubbed with a sodium carbonate solution in a modified spray dryer, the reaction product being a dry powder containing sodium sulfite and sulfate. This product is reduced with coke (or other carbon source) in a molten salt reactor. The molten product from this reactor is quenched and dissolved in water. The resulting solution is cooled, filtered, and reacted with CO_2 (from the reduction reactor) to liberate H_2S. The H_2S-rich gases are sent to a Claus plant for recovery of elemental sulfur. The carbonation generates sodium carbonate for recycle to the scrubber.

Status of Regenerable FGD Processes

Since this report deals with regenerable FGD processes, a brief review of the development status of these processes is appropriate at this point. Such a review has recently been provided by Murthy, et al.(1) This review will be highlighted in this section, with emphasis on the processes most closely related to the subject of this report.

A brief summary of the status of the regenerable processes is presented in Table A-1. Additional details on selected processes follow.

MgO Scrubbing

The magnesia scrubbing process has been shown to work with no major problems on a 100-MW coal-fired power plant boiler. The operating on-stream availability of the units was 60 percent compared to boiler on-stream time of 90 percent.(2) The Potomac Electric Power Company estimated the installed cost at $100 per kW.* Both MgO recycle possibilities and material balance (loss of MgO) were undetermined as of 1974. The unit was shut down due to the closing down of the spent magnesia regenerating plant at Rumford, Rhode Island. A 120-MW unit at the Eddystone station of Philadelphia Electric Company should be ready for operation in 1976. Economic operation of the MgO process may require a central regenerating plant for spent magnesia.

Wellman-Lord Process

The Wellman-Lord system has been successfully operated on tail gas from Claus and H_2SO_4 plants, and on oil-fired boiler flue gas but not on coal-fired boiler flue gas. Demonstration on coal-fired boilers is scheduled to start soon on a 115-MW boiler at the Dean Mitchell station of Northern Indiana Public Service Company (NIPSCO). The 85 percent concentrated SO_2 stream from the Wellman-Lord regenerator will feed an Allied Chemical SO_2 reduction process to produce >99.5 percent pure sulfur.(3) The NIPSCO estimate for capital cost is $117/kW and operating cost is 6.3 mills/kWh or 65 cents per million Btu input.

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* Costs reported in this section should be considered approximate to ±40 percent as they are highly dependent on many site and situation specific conditions.

TABLE A-1. BRIEF STATUS SUMMARY OF REGENERATIVE PROCESSES$^{(a)}$

Process Name	Year, Installation Site, Vendor, Size, and Type of Boiler	Status
MgO Scrubbing	1972, Mystic, Boston Edison, Chemico, 150 MW, oil	Shut down since June, 1974
	1974, Dickerson, Potomac Electric, Chemico, 100 MW, coal	Shut down since July, 1975
	1976?, Eddystone, Philadelphia Electric, UEC, 120 MW, coal	Shut down for modification
Wellman-Lord	1976?, D. H. Mitchell, NIPSCO, Davy Powergas/ Allied Chemical, 115 MW, coal	Under construction
Cat-Ox	1972, Wood River, Illinois Power Co., Monsanto, 110 MW, coal	Shut down since 1974
Chiyoda CT-101	1975, Scholz power plant, Gulf Power Co., Chiyoda, 23 MW, coal	Operating since June, 1975
Citrate$^{(b)}$	1973, Pfizer's Vigo Chemical complex, McKee/ Peabody, 1-MW slipstream, coal	Shut down September, 1974 after data collection

TABLE A-1. (Continued)

Process Name	Year, Installation Site, Vendor, Size, and Type of Boiler	Status
Phosphate	1974, Norwalk Harbor Station, Connecticut Power & Light Co., Stauffer, 0.1 MW, oil	Shut down June, 1974, after data collection
Catalytic-IFP	No data in open literature	No data in open literature
Consol-Potassium Salts	1972, Cromby, Philadelphia Electric Co., Consol/ Bechtel, 10 MW, coal	Shut down since 1972 after data collection (a smaller plant, 1000 acfm was operated till 1975)
AI-ACP	1971, Mohave, So. California Edison, AI, 0.5 MW, oil	Shut down 1972 after data collection on open-loop system
FW-BF	1975, Scholz power plant, Gulf Power Co., Foster Wheeler, 20 MW, coal	Started commissioning January, 1975, many problems
Westvaco	1970, Westvaco Research Center, Westvaco, 0.2 MW, oil	Shut down 1974 after data collection
SFGD	1974, Big Bend Station, Tampa Electric, Shell, 0.6-MW slipstream, coal	Tests are in progress

(a) Installations in the United States only are discussed in this table.

(b) Extensive pilot-plant studies on a lead smelter gas are being conducted by USBM Salt Lake City Metallurgy Research Center.

Citrate Process

Many versions of the Citrate process are being offered now. The Peabody Citrex process and the McKee Citrate process are based largely on the results and expertise gained from a Citrate process pilot plant operated during 1973-74 by McKee, Peabody, and Pfizer at Pfizer's Vigo Chemical complex in Terre Haute, Indiana.(4) Flue gas to the pilot plant was fed from a coal-fired boiler stack breaching. The Citrate process was pioneered by the USBM Salt Lake City Metallurgy Research Center.(5) The USBM pilot plant at Bunker Hill lead smelter, Kellogg, Idaho, is the only currently operating pilot plant. This plant employs an H_2S generator built by the Thiopet Chemical Company, Alberta, Canada, using natural gas as the feedstock. The estimated cost of full-scale Citrate process ranges from $50-60 per kW.

Phosphate (Powerclaus) Process

Stauffer's phosphate process is similar to the Citrate process in that the phosphate radical replaces the citrate radical as the hydrogen acceptor and buffering agent used to increase the solubility of SO_2 in water. The various steps in the process were tested separately at the 10 to 30 scfm level at Stauffer's Delaware City CS_2 plant. A 100 scfm pilot plant has been operated on an oil-fired boiler in Connecticut, demonstrating all features of the process except the H_2S generation. Stauffer has licensed the process to Chemico.(6)

Catalytic-IFP Process

The Catalytic-IFP process also is called the Fumeless Ammonia Scrubbing process.(7) The process promises to produce sulfur by liquid-Claus regeneration step. Details of the process status are still proprietary.

Other ammonia scrubbing processes are available, and some of these have been used for SO_2 absorption in a number of foreign plants, but in these applications the products are primarily ammonium compounds for fertilizer.

Consol Potassium Salts Process

The Consol potassium salts process is a new regenerative process which has been demonstrated on both a 1000 acfm and 30,000 acfm pilot plant. The latter pilot plant operated with flue gas drawn from a coal-fired power plant of Philadelphia Electric Company. The exact status of the process is not clear. Economics estimated by the Rust Engineering Company for 1977 startup indicate investment costs of $70/kW and operating cost of 4.1 mills/kWh.(8)

Aqueous Carbonate Process

Atomics International's aqueous carbonate process has been under development since 1970 as an alternative to AI's molten carbonate process tried earlier at the Arthur Kill Station of Consolidated Edison Company. The molten carbonate process was a victim of severe materials corrosion problems. The new process (ACP) was developed with in-house funding and shows better promise of success. The process can be used as open loop if large quantities of cheap sodium carbonate are available. If the economics dictate regeneration and closed-loop operation, AI is prepared to offer a completely closed-loop system.(9)

The entire process has not yet been tested in a single installation, but both the scrubbing system and the reduction reactor have been tested separately. The size of the reduction reactor used was equivalent to 3-5 MW of power plant capacity.

Carbon Adsorption Processes

The two carbon adsorption processes plus the Shell CuO process are the only dry processes listed in Table A-1. The Foster Wheeler-BF carbon process is the only dry process undergoing large-scale demonstration on a power plant boiler. The Westvaco process, although shown to be technically feasible from pilot-plant tests at Westvaco Research Center, is still undergoing evaluation for large-scale applicability.

Shell CuO Process

Demonstration units of the Shell process have been operated on an oil-fired process heater at a Shell refinery in The Netherlands (600 scfm) and an oil-fired boiler plus a Claus plant in Japan (79,000 scfm). Small units have been operated on slipstreams from coal-fired boilers in The Netherlands and in Florida.

Other Processes

The Cat-Ox and Chiyoda processes are not considered further here because they do not use reductants. The Cat-Ox process produces sulfuric acid and the Chiyoda process produces gypsum ($CaSO_4$). Whether the Chiyoda process should be considered a regenerable process is debatable.

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APPENDIX B

USE OF PURCHASED HYDROGEN SULFIDE

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USE OF PURCHASED HYDROGEN SULFIDE

This appendix contains the details of the study which was made of the feasibility of using purchased hydrogen sulfide as a reductant in connection with flue gas desulfurization processes. The following sections are included:

- Technical Considerations
- The Hydrogen Sulfide Market
- Geographic Considerations
- Shipping and Handling Considerations
- Conclusions.

Technical Considerations

Process Stoichiometry

The reduction of sulfur dioxide with hydrogen sulfide is the well known Claus reaction. The stoichiometry of this reaction is

$$2H_2S + SO_2 = 3S + 2H_2O.$$

On a weight basis, about one unit of hydrogen sulfide is required per unit of sulfur dioxide. On a sulfur-equivalent basis, two units of sulfur in the form of hydrogen sulfide are required to reduce one unit of sulfur in the form of sulfur dioxide. In other words, purchase of hydrogen sulfide to reduce the sulfur dioxide triples the amount of sulfur which the utility must dispose of by sale.

Properties of Hydrogen Sulfide

Physical Properties. The physical properties of hydrogen sulfide are summarized in Table B-1. The vapor pressure and density are shown as functions of temperature in Figures B-1 and B-2, respectively. Hydrogen sulfide is a gas at ambient temperatures, but it may be liquefied under

TABLE B-1. PHYSICAL PROPERTIES OF HYDROGEN SULFIDE

Color	Colorless
Corrosivity	Corrosive to eyes and respiratory tissues
Molecular Weight	34.08
Melting Point, C/F	-82.9/-117.2
Boiling Point at 14.7 psia, C/F	-60.2/-76.4
Vapor Pressure at 25.5 C	20 atm
Specific Gravity Liquid 15.5 C/15.5 C (60 F/60 F)	0.790
Density (pounds/gallon at 15.5 C)	6.58
Critical Temperature, C/F	100.4/212.7
Critical Pressure, psia	1306
Flammability Limits in Air, vol percent	4.3-46 percent
Cp Vapor (Btu/lb) at 15.5 C and 14.7 psia	0.254
Cv Vapor (Btu/lb) at 15.5 C and 14.7 psia	0.192
Cp Liquid (Btu/lb) at -46 to -18 C (-50 to 0 F)	0.454
At 15.5 C and 14.7 psia	0.532
Auto Ignition Temperature, C/F	260/500
Heat of Vaporization (Btu/lb) at -60.2 C (-76.4 F) and 14.7 psia	236.3
15.5 C (60 F) and 229 psia	191.1

Source: Stauffer Chemical Company, "Safe Handling of Liquid Hydrogen Sulfide".

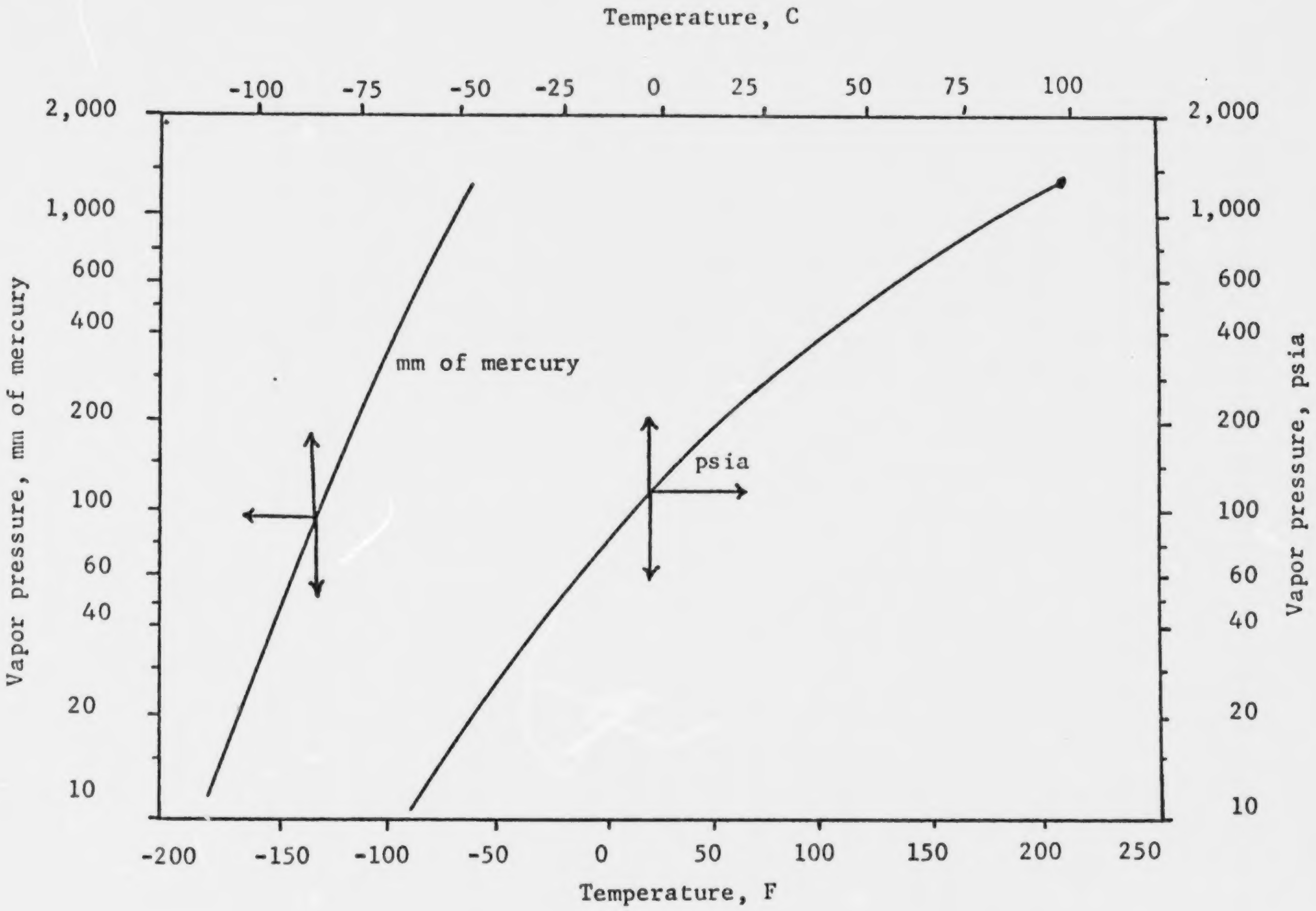

FIGURE B-1. H_2S VAPOR PRESSURE VERSUS TEMPERATURE

Source: Stauffer Chemical Co., "Safe Handling of Liquid Hydrogen Sulfide".

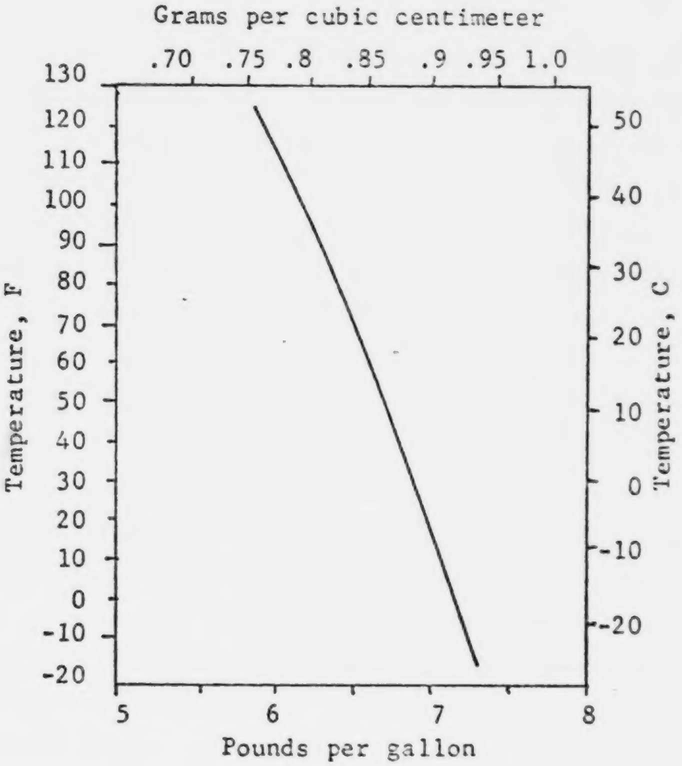

FIGURE B-2. H_2S DENSITY VERSUS TEMPERATURE pressure. The vapor pressure of hydrogen sulfide is higher than that of ammonia and propane but lower than carbon dioxide. This means that stronger tanks would be required to ship and store hydrogen sulfide than are used for ammonia to liquefied petroleum gases.

Toxicity. Hydrogen sulfide is a highly toxic gas, extremely dangerous in very low concentrations. The threshold limit value for hydrogen sulfide is 10 ppm as defined by the American Conference of Governmental Industrial Hygienists. This represents the condition under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effects. It is both an irritant and an asphyxiant and may be characterized by its repugnant odor of "rotten eggs". The toxic hazard is aggravated because unprotected exposure to nontoxic levels of hydrogen sulfide will result in temporary olfactory fatigue and can give a false sense of security in dangerous concentrations.

As the concentration increases (200-500 ppm), effects on the nervous system become pronounced. Headaches, dizziness, excitement, staggering gait, and diarrhea are some of the results that occur. Bronchitis or bronchial pneumonia may also follow.

The nervous system response reverses as hydrogen sulfide concentration increases. While at lower concentrations it may be a depressant, at higher values, it stimulates. Still higher values will paralyze the respiratory center.

The acute effects of hydrogen sulfide inhalation represent the most serious threat in handling. Although it is not a cumulative poison, severe exposure may result in brain damage from oxygen deficiency if breathing is not rapidly regained. Permanent olfactory damage (loss of sense of smell) may result from extended exposure at less than lethal levels. Exposures in the 700-1000 ppm range may be fatal in 30 minutes. Very high concentrations will be instantly fatal.

The effects of hydrogen sulfide on humans are summarized in Table B-2. Liquid hydrogen sulfide poses another hazard in that contact with the skin can result in severe frost bite.

Trained operating personnel at chemical plants and petroleum refineries can handle large volumes of toxic materials like hydrogen

TABLE B-2. ACUTE EFFECTS OF HYDROGEN SULFIDE GAS

Hydrogen Sulfide, H_2S		
Concentration, ppm	Time	Effect
0.13	Sniff	Odor detectable
10.0	8 hours	Threshold limit
50-100	1 hour	Mucous membrane irritation
200-300	1 hour	Mucous membrane irritation (severe)
500-700	1/2 hour	Coma
900	Minutes	May be fatal
1000	Minutes	Fatal

Source: Stauffer Chemical Co., "Safe Handling of Liquid Hydrogen Sulfide".

sulfide without undue hazard. Operating and other personnel at electricity generating plants are not trained to handle such hazardous materials. The magnitude of the potential safety problems cannot be discounted. The toxicity of hydrogen sulfide may cause problems at power plants.

Corrosion Properties. Severe corrosion and cracking problems in piping and storage vessels are experienced if water in any significant amount is associated with the hydrogen sulfide. The hydrogen sulfide in combination with water can attack metals and their oxidation products in storage vessels or piping to form sulfide, which is hazardous due to its pyrophoric nature. Stress cracking is also a direct result of these conditions.

All metallic portions anticipated for use in a liquid hydrogen sulfide system should be carefully reviewed in the light of the publication of the National Association of Corrosion Engineers.(1) This publication is considered to be one of the most comprehensive studies of the sulfide stress cracking phenomenon and should be considered basic to the reference material for any plant using liquid hydrogen sulfide.

Hydrogen sulfide piping generally is constructed of 316 Stainless Steel to minimize the corrosion problems. The corrosion properties of hydrogen sulfide are severe enough to cause great concern for any potential power plant use. For these reasons, the installation cost of equipment to handle hydrogen sulfide and the cost of the special materials, monitors, and precautions required because of the corrosive nature of hydrogen sulfide are an important consideration in evaluating the potential use of this reductant.

Fire and Explosive Properties. The flammable or explosive range for hydrogen sulfide gas in air is 4.3-46 percent by volume. The vapor is slightly heavier than air, which permits the gas to "pocket" in "still" conditions. The auto-ignition temperature in air of hydrogen sulfide is 500 F. For this reason, all sources of ignition such as open flames, sparks, glowing surfaces, and all electrical equipment should be protected to prevent contact with the gas. Only non-sparking tools should be used in areas where hydrogen sulfide is handled.

The Hydrogen Sulfide Market

Supply

Hydrogen sulfide currently is a specialty chemical with a limited market. The current market and distribution system would not suffice for large scale uses like flue gas desulfurization. Therefore, historic data are of little use in analyzing supply.

Potential Supply

Although there are some specific processes for the manufacture of hydrogen sulfide, most hydrogen sulfide is recovered from either natural gas or from refinery gas streams. The hydrogen sulfide is removed from these gas streams by absorption in an alkaline solution, generally an ethanol amine. Concentrated hydrogen sulfide is then recovered by stripping the amine solution. The hydrogen sulfide generally is converted into sulfur, although at some small gas processing plants it may be flared.

The largest potential sources of hydrogen sulfide are petroleum refineries and natural gas processing plants. In the future, hydrogen sulfide also may be available at coal gasification plants and coal desulfurization plants using hydrodesulfurization (for example, the solvent-refined coal process). In 1973, refineries converted hydrogen sulfide recovered from process streams into an estimated 5,330 metric tons* sulfur per day.(2) The hydrogen sulfide removed from refinery gases is generally converted to sulfur in the refinery. The two major sources of hydrogen sulfide in the refinery are fuel gases and recycle streams from hydrogen processing operations. There are also a few minor sources of hydrogen sulfide in refineries like sour water strippers. In the past, much of the hydrogen sulfide in fuel gas has not been recovered.

The quantity of hydrogen sulfide removed from process streams is expected to increase significantly due to environmental regulations requiring removal of hydrogen sulfide from refinery fuel gases. It is estimated that the total hydrogen sulfide generated at refineries in 1973 was 11,000 metric tons sulfur equivalent per day and 11,500 in 1974. The unrecovered 6000 metric tons per day will be recovered as soon as regulations limiting sulfur content of refinery fuel gas become effective. Furthermore, the higher sulfur content of crude oil processed in U.S. refineries, increased refining capacity, and increased hydrodesulfurization will result in increased hydrogen sulfide recovery. It is estimated that by 1980 the recovery of hydrogen sulfide at refineries will increase to the equivalent of 17,700 metric tons per day (see Table B-3).

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* A metric ton equal to 2205 pounds. A long ton, which is the standard unit of measure in the sulfur industry, is 2240 pounds. A ton in this report refers to a short ton of 2000 pounds.

The second largest source of hydrogen sulfide is natural gas processing plants. In 1973, it is estimated that the average sulfur production from these sulfur plants was 2,440 metric tons per day.(3) It may be noted that this is significantly higher than the 1,740 metric tons per day reported in the literature. The higher estimate was based on industry contacts. It is believed that reported production omits some significant plants.

In addition to the sulfur recovered at the natural gas processing plants, there is an estimated 1,230 metric tons per day hydrogen sulfide removed at small gas plants which is not converted to sulfur. This hydrogen sulfide currently is burned and vented to the atmosphere. It is uneconomic to recover as sulfur, but it might be liquefied and sold if a suitable market were developed. If future regulations prohibit flaring of hydrogen sulfide, sale of hydrogen sulfide would probably be more attractive than making sulfur at these small plants.

Natural gas production in the lower 48 states is expected to decline in the future. The sulfur content of new gas fields is not known. There will probably be environmental pressure to flare less hydrogen sulfide at gas plants. In view of these uncertainties, it has been assumed that the production and availability of hydrogen sulfide from gas plants will remain constant through 1980 (see Table B-3).

It should be noted that there is some discrepancy between statistics on hydrogen sulfide availability. The U.S. Bureau of Mines reports recovered elemental sulfur, which includes both petroleum refineries and natural gas processing plants, in 1973 was 2.4 million metric tons. This is equivalent to 6,619 metric tons per day, somewhat below the estimated 7,770 metric tons per day (5,330 from refineries plus 2,440 from natural gas

TABLE B-3. ESTIMATED H_2S AVAILABLE FROM OIL AND GAS PROCESSING

	1974	1980 (est.)
Average sulfur content of crude oil, wt. %(a)	0.88	1.07
Crude oil processing rate, 10^6 bbl/D	12.9(b)	16.6
Natural gas processing rate, 10^9 SCF/D	55.6(c)	55.6
Total H_2S produced, 10^3 Met tons/D		
Oil refineries(d)	11.5	17.7
Natural gas plants(e)	3.7	3.7
Total	15.2	21.4
H_2S sent to Claus plants, 10^3 Met tons/D		
Oil refineries(f)	5.6	17.7
Natural gas plants(e)	2.4	2.4
Total	8.0	20.1

(a) NPRA Survey, Letter from D. C. O'Hara to R. E. Train (EPA), August 30, 1974.

(b) Oil and Gas Journal, 72, April 1, 1974, plus crude run/capacity ratios from Oil and Gas Journal, 1970-1974.

(c) Oil and Gas Journal, 72, July 8, 1974.

(d) Based on average crude oil density of 301 lb/B and 70 percent S in crude going to H_2S.

(e) Murthy, K. S., BCL report on EPA Contract 68-02-0611, August 28, 1974. (See Reference 3.)

(f) Based on 70 percent utilization of capacity; capacity based on Beers, W. D., "Characterization of Claus Plant Emissions", Process Research, Inc., Report No. EPA R2-73-188, April, 1973.

plants) discussed above. A small portion of this discrepancy may be due to a portion of the hydrogen sulfide being converted directly to sulfuric acid or sold as hydrogen sulfide. These probably account for less than 500 metric tons per day. The higher estimate is believed to be more accurate.

As mentioned earlier, it is expected that coal desulfurization and coal gasification plants may provide additional potential sources of hydrogen sulfide. In particular, in the event of coal gasification located at an electric utility, enough hydrogen sulfide would be recovered to satisfy the needs of a coal-burning generation facility of twice the capacity of the gas burning facility. Although these coal-processing plants may be a significant local source of hydrogen sulfide for a specific power plant, their contribution to the national production will be insignificant through 1985.

Historic Supply

The historic supply of hydrogen sulfide has little bearing on the potential supply for pollution abatement uses. Hydrogen sulfide is used mainly for the manufacture of alkali sulfides, which are used in the dye and leather industries. There are also other minor uses. The Bureau of Mines reports that between 1969 and 1973 the total production of sulfur dioxide and hydrogen sulfide varied between 88,000 and 149,000 metric tons per year sulfur equivalent.(5) Industry sources indicate that these data may be in error, but in any event the total sales of hydrogen sulfide are small.

The major merchandiser of hydrogen sulfide is the Stauffer Chemical Company, which shipped approximately 29,000 metric tons of hydrogen sulfide in 1973. The second producer is the Montana Sulphur and Chemical Company, which shipped between 5,440 and 6,350 metric tons of hydrogen sulfide in 1973. PPG Industries and a few other companies sell small quantities of hydrogen sulfide in cylinders. Most of the hydrogen sulfide sold in the United States originates at petroleum refineries.

Thio-Pet Chemicals Ltd. operates a petrochemical plant at Fort Saskatchewan, Alberta for manufacture of carbon disulfide and hydrogen sulfide by-product by the methane-sulfur process.(6) The Thio-Pet plant commenced operations in spring 1965 with an initial daily hydrogen sulfide capacity of 8 tons and was expanded in 1967 to a hydrogen sulfide capacity of 13 tons per day. A portion of the hydrogen sulfide by-product is sold by pipeline to an adjacent chemical plant as an impure vapor at 150 psig. Facilities for production of purified hydrogen sulfide liquid product were put in service in December 1965. Pure liquid hydrogen sulfide is marketed in pressure cylinders and in bulk by railroad tank cars. The first tank car shipment was made in June 1966.

Hydrogen sulfide produced by Thio-Pet is a by-product of the methane-sulfur carbon disulfide process represented by the following equation:

$$CH_4 + 4S \longrightarrow CS_2 + 2H_2S.$$

This reaction is carried out over a catalyst at high temperature and low pressure. It is customary for the hydrogen sulfide by-product to be reconverted to sulfur by the modified Claus process and to recycle the sulfur recovered from the by-product hydrogen sulfide to the carbon disulfide reactor. Reconversion of hydrogen sulfide to sulfur was not, however, economically justified for the Thio-Pet operation because of the relatively small capacity of the plant. Instead, the hydrogen sulfide is purified to varying degrees and sold as both vapor and liquid.

Demand

The demand for hydrogen sulfide to reduce all the SO_2 which could be recovered from power plant flue gas far exceeds the potential supply of hydrogen sulfide. The total emissions of SO_2 from power plants in the United States in 1970 was about 19.4 million tons.(7) Between 1960 and 1970 these emissions had increased at an average rate of about 6.7 percent per year.(7) If this rate were to continue, the potential (uncontrolled) SO_2 emissions in 1980 would be about 37 million tons. To reduce emissions some power plants have recently switched to lower sulfur fuels. For example, the average sulfur content of coal burned at power plants decreased from about 2.6 percent in 1969 to 2.3 percent in 1972.(8) On the other hand, the shortage of natural gas will almost certainly result in a decrease in the consumption of this fuel at power plants, and conversion to other fossil fuels will increase the SO_2 emissions. In spite of the uncertainty in the potential SO_2 emissions, the following calculation illustrates the point. A total SO_2 emission of only 25 million tons per year would require about 66,100 metric tons of H_2S per day for reduction. This is about 3.3 times the estimated potential H_2S supply in 1980 (see Table B-3). Looking at it in the other direction, there is potentially enough hydrogen sulfide available to reduce about one third of the SO_2 produced at power plants.

Requirements for 1000-MW Power Plant

A 1000-megawatt power plant operating at full load on 3.5 percent sulfur coal and recovering 90 percent of the SO_2 from the flue gas will require about 10,600 scfm of reductant (based on 2 moles of reductant per mole of SO_2). If H_2S is used, this equivalent to about 658 metric tons per day. If the H_2S was received in liquefied form, the requirement would be about 805,000 liters (213,000 gallons) per day. Using present shipping practices (see section on Shipping), this corresponds to about 10 railroad tank cars per day.

Prices

There are currently only two significant marketers of hydrogen sulfide, Stauffer Chemical Company and Montana Sulfur and Chemical Company. Stauffer's current list price is $0.10 per pound (220 dollars per metric ton). Montana Sulfur quotes the price of $0.065 per pound (143 dollars per metric ton), and most hydrogen sulfide is probably sold at the lower figure.

The current prices have little relevance to the price of the large volumes of hydrogen sulfide that might be required by an electric utility. Such purchases will probably be made on a long-term contract, with the price of hydrogen sulfide, f.o.b. refinery, equal to or slightly less than the price of contained sulfur.

The market value of sulfur is quite volatile. In recent years, the price of recovered sulfur, f.o.b. plants, has ranged from $29.15 per metric ton in 1969 to $15.45 in 1973.(5) In 1974, prices increased rapidly. For example, the average export value for the first 7 months of 1974 was $32.63 per metric ton, compared with $19.38 in 1973. For the month of July, the value of export shipments was $41.61 per metric ton.(9)

Because a refinery or large natural gas processing plant converts recovered hydrogen sulfide into sulfur, they should be indifferent to selling the sulfur in elemental form or as hydrogen sulfide, provided they can obtain an equivalent price. In most cases, by the time a utility decided to purchase hydrogen sulfide from a refinery, the refinery would have already invested in the sulfur plant. Therefore, the price of hydrogen sulfide would have to cover depreciation and return on investment on the sulfur plant and perhaps on a sulfur-plant tail-gas treating unit. In order to sell hydrogen sulfide, the refiner will have to install liquefaction, pumping, storage, and shipping facilities. The price of hydrogen sulfide will have to include depreciation and return on investment on these new investments as well as on the existing sulfur plant. Because hydrogen sulfide and sulfur are generally considered a nuisance by-product by refiners, in times of low-sulfur prices the refiner may be willing to accept less than an "adequate" return on investment. Another factor to consider is the additional tail gas cleanup which will be required under EPA regulations. A refiner may be willing to sell H_2S at a loss instead of investing in cleanup facilities for Claus plants.

The existing refiner will have the option of either selling hydrogen sulfide or manufacturing and selling sulfur. Thus, the minimum price of hydrogen sulfide, on a contained sulfur basis, would be the price of sulfur less direct operating expenses for sulfur manufacture plus the cost of handling and shipping hydrogen sulfide. The direct manufacturing expenses are estimated to be between $6 and $18 per metric ton.

Since high-purity H_2S is not required for reduction purposes, gasification of coal or residual oil may prove feasible as a source of H_2S. In Section 11 of this report it is estimated that the cost of producing H_2S via gasification of coal or residual oil would be between 2.5 and 3.2 cents per pound ($55-71/metric ton) of H_2S, depending on the feedstock cost and plant size. Thus, a power plant having access to an "across the fence" source of H_2S would probably need to purchase H_2S at these price levels or lower to prove economically attractive.

Geographic Considerations

The major sources of hydrogen sulfide supply are not necessarily located near electric utilities. The U.S. petroleum refineries and their sulfur plant capacities are summarized in Table B-4 and the natural gas processing plants and associated sulfur production are summarized in Table B-5. From these tables it can be seen that the greatest potential for production of hydrogen sulfide exists in California, Texas, Louisiana, New Jersey, Pennsylvania, and Delaware. In general, petroleum refineries are apt to be located near power generation plants while gas processing plants are more likely to be in isolated areas.

Electric power generation plants are generally located near population centers. The location of the major coal and oil-fired power plants is illustrated in Figure B-1. The power plants located near Chicago, Toledo, Philadelphia, Los Angeles, San Francisco, and in New Jersey and Delaware and a few in the Ohio River Valley are apt to be located very near petroleum refineries. Rather short pipelines (10 miles or less) would probably be the most practical means to deliver hydrogen sulfide to power plants in these areas. Power plants in other areas would have to obtain hydrogen sulfide either by rail or barge. For power plants located farther from refineries or natural gas processing plants, transportation costs could significantly affect the overall economics of flue gas desulfurization using hydrogen sulfide as a reductant.

Another important geographic factor concerns the market for sulfur. The largest market is in the Gulf Coast states, especially Florida where the phosphate fertilizer industry is concentrated. In 1971,

TABLE B-4. REFINERY CLAUS PLANT CAPACITIES

State	Crude Oil Capacity[a], 1000 Met tons/D	Claus Plant Capacity[b], Met tons Sulfur/D
Alabama	5.31	--
Alaska	7.33	9
Arkansas	6.55	25
California	234.60	2556
Colorado	6.76	18
Delaware	19.15	782
Florida	0.68	--
Georgia	1.68	--
Hawaii	8.66	--
Illinois	142.48	572
Indiana	73.54	425
Kansas	52.94	44
Kentucky	21.68	--
Louisiana	212.21	585
Maryland	3.27	--
Michigan	18.11	91
Minnesota	23.71	174
Mississippi	41.90	30
Missouri	14.09	80
Montana	18.95	115
Nebraska	0.68	--
New Jersey	80.98	622
New Mexico	6.46	30
New York	14.04	50
North Dakota	7.22	207
Ohio	79.89	90
Oklahoma	63.12	--
Oregon	2.26	--
Pennsylvania	88.63	345
Rhode Island	1.03	--
Tennessee	3.97	--
Texas	477.10	1207
Utah	16.59	12
Virginia	6.57	50
Washington	46.39	--
West Virginia	2.67	--
Wisconsin	4.86	15
Wyoming	19.53	--
TOTAL	1,835.59	8,134

(a) Based on crude oil density of 301 lb/bbl (1 metric ton = 7.31 bbl). January 1, 1974 data.

(b) Beers, W. D., "Characterization of Claus Plant Emissions", Process Research, Incorporated, Report No. EPA-R2-73-188, April, 1973. Added 5 percent for "greater than" figures.

TABLE B-5. SALIENT DATA ON SULFUR RECOVERY IN NATURAL GAS PROCESSING(a)

	Associated (Sour) Gas Throughput, 10^6 scf/D	Total Sulfur Production, Met tons/D
Arkansas	31.9	5.3
Florida	130	650
Mississippi	20	221.4
New Mexico	54.3	30
North Dakota	74.8	116
Texas	783.0	1,320.6
Wyoming	68.2	100
Total	1,162.2	2,443.3

(a) Source: Murthy, K. S. (Reference 3.)

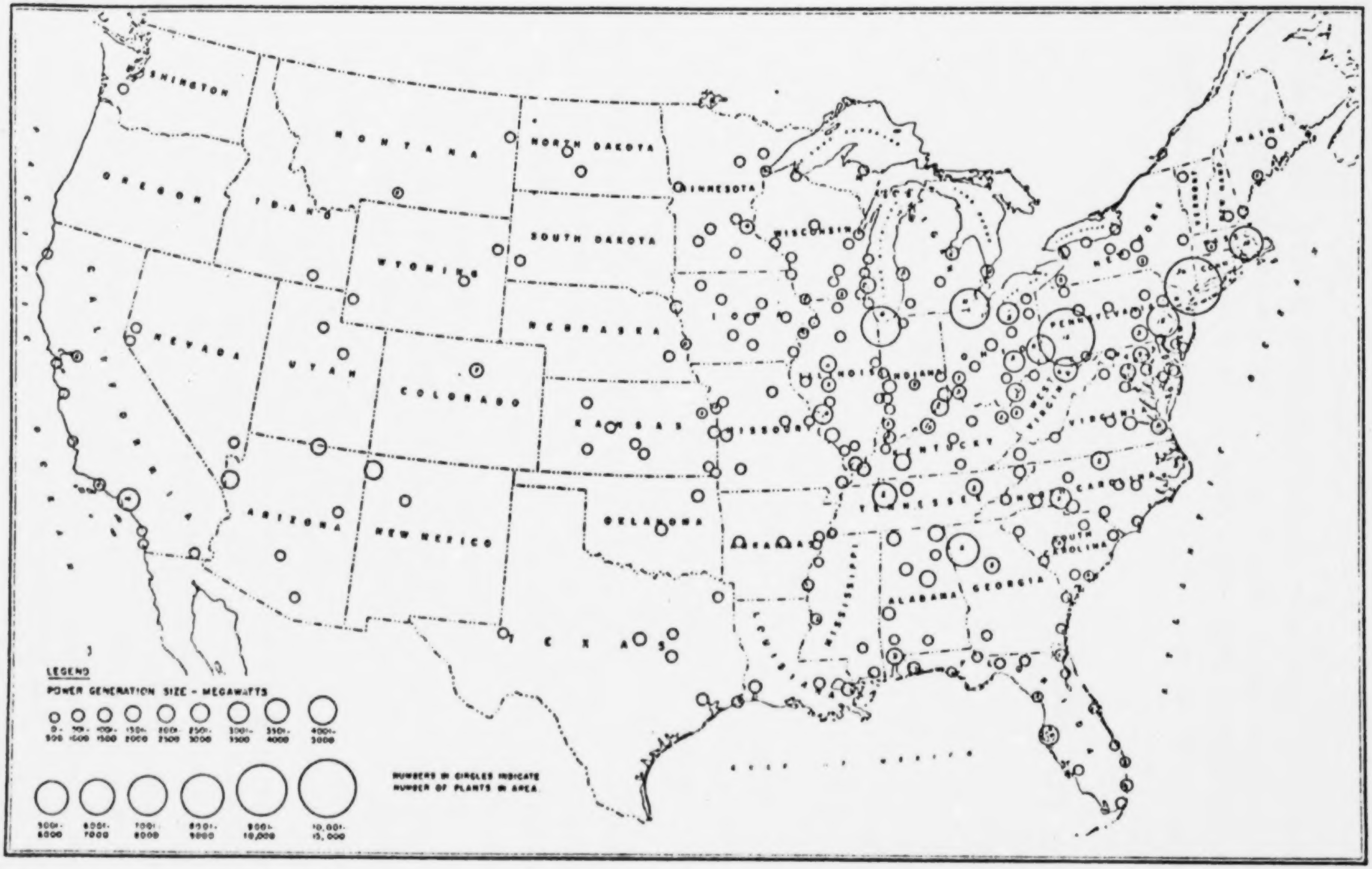
WASHINGTON
OREGON
CALIFORNIA
NEVADA
IDAHO
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
WISCONSIN
MISSOURI
ARKANSAS
LOUISIANA
MISSISSIPPI
ALABAMA
GEORGIA
TENNESSEE
KENTUCKY
INDIANA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
WEST VIRGINIA
PENN.
NEW YORK
MAINE
LEGEND
POWER GENERATION SIZE - MEGAWATTS
0-500
501-1000
1001-1500
1501-2000
2001-2500
2501-3000
3001-3500
3501-4000
4001-5000
5001-6000
6001-7000
7001-8000
8001-9000
9001-10,000
10,001-15,000
NUMBERS IN CIRCLES INDICATE NUMBER OF PLANTS IN AREA

FIGURE B-1. LOCATION OF MAJOR COAL- AND OIL-FIRED POWER UNITS - 1971

Source: McGlamery, G. G., et al.(10)

10,630 metric tons sulfur per day were consumed in Florida, Louisiana, and Texas. Transportation costs to ship sulfur from the power plant to customers can greatly affect the economics of a given project (3 metric tons sulfur are produced per metric ton sulfur removed from flue gas).

Shipping and Handling Considerations

Shipping

In the section on Technical Considerations, the extremely toxic, corrosive, and explosive nature of hydrogen sulfide was discussed.

In principle, liquefied hydrogen sulfide can be shipped by tank truck, railroad car, barge, or pipeline. The toxic and corrosive nature of hydrogen sulfide place severe limitations on the use of these transportation modes. At the present time, liquefied hydrogen sulfide is only transported by tank truck or railroad car at a cost of approximately 3 to 4 cents per metric ton-mile. Barge transportation would probably cost somewhat less but would be of quite limited applicability. Pipeline transportation probably is impractical for all except very short distances because special lined or stainless steel pipelines would be required to avoid corrosion.

The Code of Federal Regulations classifies hydrogen sulfide as a flammable compressed gas (49 CFR 170.1, P 172.5) and shippers should conform with applicable DOT regulations. For tank car shipments the Code requires a pressure vessel classified as DOT-106A800X. These are multiunit tank car tanks which are designed to be removed from the car structure for filling and emptying. The maximum allowable water capacity of each tank is 2600 pounds. For hydrogen sulfide the maximum permitted filling density is 68 percent; this would give each tank a maximum capacity of 1768 pounds hydrogen sulfide.

Compliance with the above Code would be impractical for bulk shipments. Both U.S. companies that ship hydrogen sulfide in bulk have a special permit from the Department of Transportation to use DOT-105A-600W tank cars with a maximum loading capacity of approximately 70 tons, or tank trailers with a capacity of approximately 14 tons. The DOT permit is valid for 2 years. Renewal is contingent upon providing the Department of Transportation with satisfactory reports on safety inspections, total shipments, and any accidents that may have occurred.

Storage

Whether the hydrogen sulfide is received by the power plant as a liquid from shipping vessels or as a gas piped from a nearby source, sufficient storage capacity must be provided to insure continuous operation. It is believed that a minimum supply for 15 days of operation should be on hand. For a 1000-megawatt plant burning coal containing 3.5 percent sulfur, it is estimated that a total storage capacity for close to 10,000 metric tons of hydrogen sulfide to be necessary. If the hydrogen sulfide were to be shipped in railroad tank cars of present size, approximately 10 cars would be needed every day.

The volume occupied by 10,000 metric tons of liquefied hydrogen sulfide is approximately 11,436 cubic meters (413,800 cubic feet) at room temperature. The storage and handling of liquefied hydrogen sulfide is complicated by the fact that the material must be kept under pressure. The vapor pressure is 18 atmospheres at 21 C (70 F) and 31 atmospheres at 43 C (110 F). Also, special precautions must be taken to avoid problems due to corrosion, particularly sulfide stress cracking. This is treated rather extensively in Reference 1.

Even if a power plant would receive hydrogen sulfide by pipeline, similar though somewhat less storage would be required. Hydrogen sulfide would be produced in refineries at a relatively steady rate. The demand by the power plant could fluctuate by daily, weekly, and seasonal cycles.

The H_2S storage requirements could be reduced, albeit at the expense of more H_2S consumption, by providing an incinerator in which some H_2S could be burned and then sent through the FGD system at times wnen the H_2S supply got ahead of the power plant demand.

Conclusions

Hydrogen sulfide presently is marketed on a very modest scale, and the market is not expected to expand significantly through 1985. However, a large-scale use (such as flue gas desulfurization) would require a vastly expanded supply which would involve oil refineries and some natural gas processing plants. The potential supply of hydrogen sulfide from these sources is sufficient to handle only a portion of the power plants which will be installing flue gas desulfurization systems.

Geographical considerations will further restrict the use of hydrogen sulfide at power plants. The present and potential sources of hydrogen sulfide are concentrated in the South and the West. In contrast, the demand for electricity is concentrated in the population density centers of the East and Midwest. Since the costs of shipping hydrogen sulfide are relatively high (approximately 3-4 cents per metric ton-mile), the use of hydrogen sulfide as a reductant gas is not expected to be feasible when the transportation distances exceed a few hundred miles. Some use of hydrogen sulfide may be practical for power plants located near refineries or sour gas wells.

It is concluded that purchased or merchant hydrogen sulfide will play only a minor role as a reductant for sulfur dioxide from FGD systems.

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APPENDIX C

GASIFICATION PROCESSES

APPENDIX C

GASIFICATION PROCESSES

This appendix contains additional information on the coal and oil gasification processes discussed in the text. The following processes are included:

Coal Gasification

(1) Koppers-Totzek gasifier
(2) Wellman-Galusha gasifier
(3) Winkler gasifier
(4) Riley-Morgan gasifier

Oil Gasification

(1) Shell Gasification Process
(2) Texaco Synthesis Gas Generation Process.

Coal Gasification Processes

Koppers-Totzek Gasifier(1,2)

The Koppers-Totzek gasifier, shown schematically in Figure C-1, is an oxygen blown, atmospheric pressure, entrained system. Over 50 gasifiers of this type have been built. In this system, pulverized coal, 90 percent under 200 mesh, is screw fed from hoppers into pairs of burners situated opposite each other on the same axis so that their jet discharges converge. A gasifier may contain two or four such burner heads. Oxygen conveys the coal from the screw feeders to the burner nozzles at velocities sufficient to prevent flame propagation into the feeder tubes (300 ft/sec). Coal is dried to about 1 weight percent moisture, but moisture contents of 4 to 8 weight percent can be tolerated. The gasifier is refractory-lined with a water jacket where process steam is raised and added to the burner nozzles in amounts sufficient to maintain the flame temperature at about 1930 C (3500 F). The gas temperature at the reactor exit is about 1480 C (2700 F). About 50 percent of the coal ash

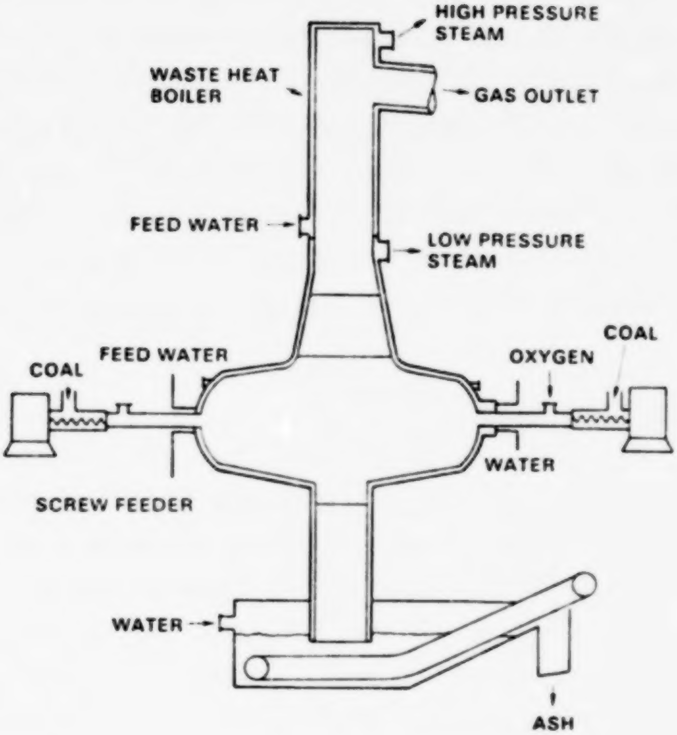
HIGH PRESSURE STEAM
WASTE HEAT BOILER
GAS OUTLET
FEED WATER
LOW PRESSURE STEAM
COAL
FEED WATER
OXYGEN
COAL
WATER
SCREW FEEDER
WATER
ASH

FIGURE C-1. THE KOPPERS-TOTZEK GASIFIER

leaves as slag which is quenched and granulated in water at the bottom of the reactor, and 50 percent leaves as fly ash with the product gas and is removed in gas cleanup. Waste heat boilers are used to recover the sensible heat in the high temperature product gas. The gas is further cooled and cleaned by conventional, commercially proven processes.

The gasifier thermal efficiency (70 to 80 percent) will be lower if the sensible heat in the product gas is not recovered. Essentially no methane is produced in the gasifier. Gasifier outputs and typical raw gas composition for different coals are shown in Table C-1. The K-T gasifier is highly sophisticated in its design and operational aspects and hence can be more reliable in operation but at a higher cost than other gasifiers.(3)

The Wellman-Galusha (W-G) Gasifier(1,4)

The W-G gasifier (Figure C-2) employs a fixed bed and operates similar to the Lurgi gasifier but at atmospheric pressure with air or oxygen. The product gas heating value is 290 Btu/scf when oxygen blown. Gas cleaning systems offered include the Holmes-Stretford system offered by the Peabody Engineered Systems, Stamford, Connecticut.

Complete system design and construction services are offered by A. G. McKee, Cleveland, Ohio, and Mason & Hanger-Silas Mason Co., Inc. The McDowell-Wellman Company, Cleveland, Ohio, offers only the gasifier. Presently, seven air-blown commercial units are operating in the U.S. Typical composition of Wellman-Galusha gas from air- and oxygen-blown systems is presented in Table C-2.

Winkler Gasifier(1,5)

The Winkler process is a commercially proven, fluidized-bed, atmospheric pressure system for the production of synthesis gas from coal. An air-blown version of the Winkler gasifier is available from Davy Powergas of Lakeland, Flordia. A typical gasifier is shown in Figure C-3.

The generator is a cylindrical, refractory-lined vessel, 12 to 18 feet in diameter and 65 feet high. Coal usually is crushed to

TABLE C-1. K-T GASIFIER DATA FOR U.S. COALS

	Western Coal	Illinois Coal	Eastern Coal
Gasifier Feed			
Dried coal to gasifier analysis, weight percent			
C	56.76	61.94	69.88
H	4.24	4.36	4.90
N	1.01	0.97	1.37
S	0.67	4.88	1.08
O	13.18	6.73	7.05
Ash	22.14	19.12	13.72
Moisture	2.00	2.00	2.00
Gross heating value, Btu/lb	9,888.0	11,388.0	12,696.0
Oxygen, ton/ton dried coal	0.649	0.704	0.817
Purity, percent	98.0	98.0	98.0
Process steam, lb/ton dried coal	272.9	541.3	587.4
Gasifier Products			
Jacket steam, lb/ton dried coal	347.8	404.9	464.9
High pressure steam, lb/ton dried coal	2,147.1	2,292.2	3,023.6
Raw Gas			
Analysis (dry basis), volume percent			
CO	58.68	55.38	55.90
CO_2	7.04	7.04	7.18
H_2	32.86	34.62	35.39
N_2	1.12	1.01	1.14
H_2S	0.28	1.83	0.35
COS	0.02	0.12	0.04
	100.00	100.00	100.00

Source: Reference 1.

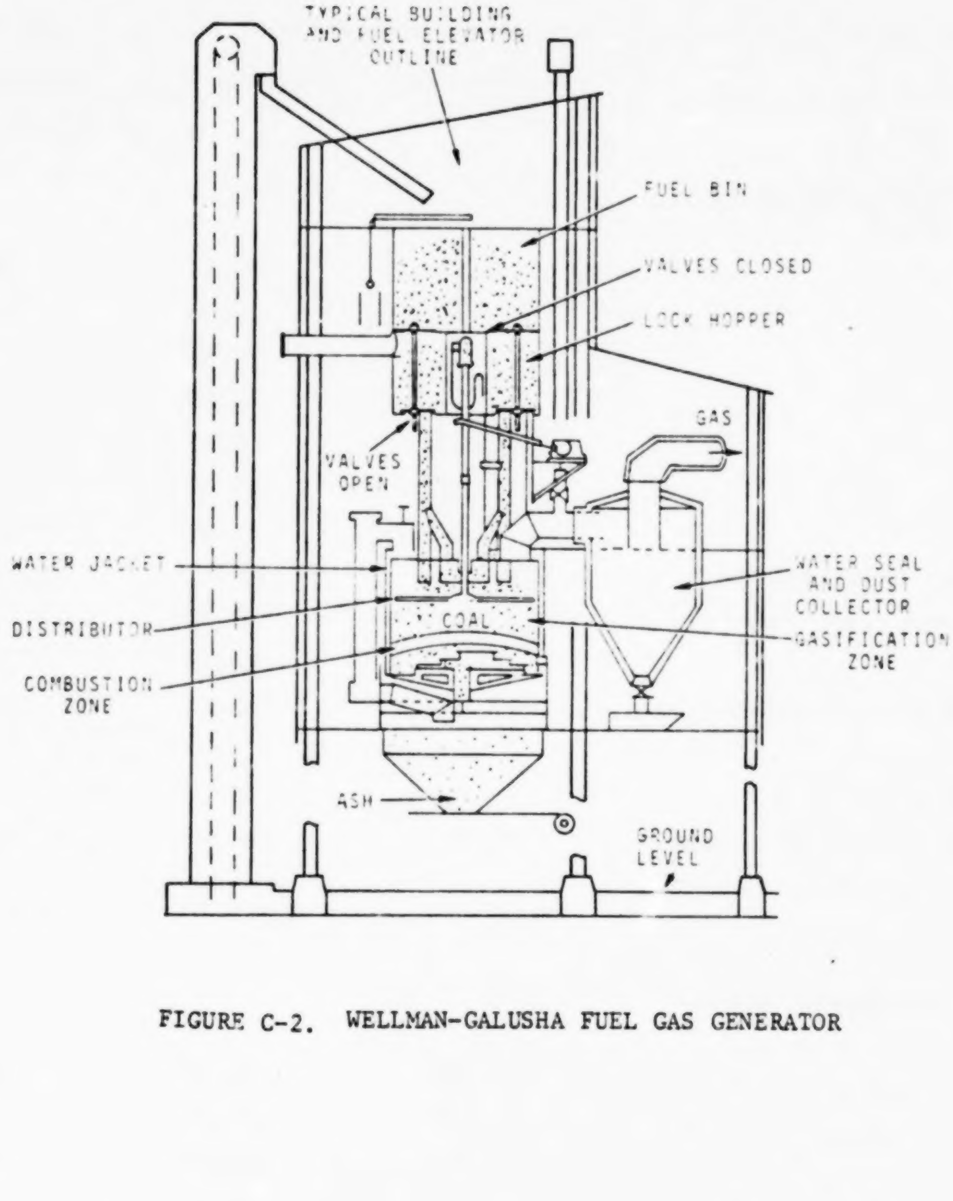
TYPICAL BUILDING AND FUEL ELEVATOR OUTLINE
FUEL BIN
VALVES CLOSED
LOCK HOPPER
GAS
VALVES OPEN
WATER JACKET
WATER SEAL AND DUST COLLECTOR
DISTRIBUTOR
COAL
GASIFICATION ZONE
COMBUSTION ZONE
ASH
GROUND LEVEL

FIGURE C-2. WELLMAN-GALUSHA FUEL GAS GENERATOR

TABLE C-2. TYPICAL WELLMAN-GALUSHA PRODUCER GAS COMPOSITIONS

Composition (dry basis), volume percent	Air-Steam Mode			Oyxgen-Steam Mode	
	Bituminous Coal	Anthracite Coal	Coke	Anthracite Coal	Coke
CO	28.6	27.1	29.0	42.0	54.0
H_2	15.0	16.6	10.0	39.0	31.0
CO_2	3.4	5.0	3.5	17.0	11.3
CH_4	2.7	0.5	0.7	0.7	0.4
O_2	0	0	0	0.2	0.6
N_2	50.3	50.8	56.8	1.1	2.7

Source: Telephone conversation with Mr. David D. Woodruff, General Sales Manager, McDowell-Wellman Engineering Company, Cleveland, Ohio, for oxygen-blown systems data. Air-blown data are from Reference 22.

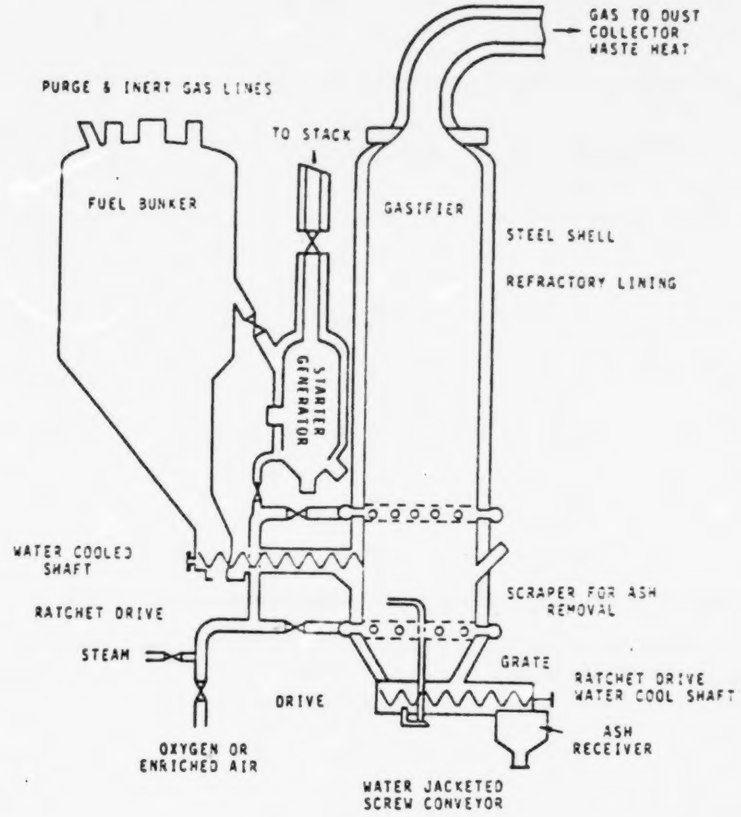
GAS TO DUST
COLLECTOR
WASTE HEAT
PURGE & INERT GAS LINES
TO STACK
FUEL BUNKER
GASIFIER
STEEL SHELL
REFRACTORY LINING
STARTER GENERATOR
WATER COOLED
SHAFT
SCRAPER FOR ASH
REMOVAL
RATCHET DRIVE
STEAM
GRATE
RATCHET DRIVE
WATER COOL SHAFT
DRIVE
ASH
RECEIVER
OXYGEN OR
ENRICHED AIR
WATER JACKETED
SCREW CONVEYOR

FIGURE C-3. WINKLER GASIFIER

0-3/8 in. and dried, although moisture contents of up to 18 percent can be tolerated. Coal is fed to the generator through variable speed screws which serve as seals to prevent back flow of gases. The gasifying medium fluidizes the coal bed and gasifies the coal at a uniform temperature. Oxygen (or air)-steam mixtures are added at the bottom and top of the bed. The highest temperatures in the system occur at the top of the fluid bed. Typical gas compositions for oxygen-blown operation are shown in Table C-3.

Ash leaves the generator with the product gas (70 percent) and at the bottom of the fluid bed (30 percent). Particles that leave as fly ash are sometimes molten since the maximum temperature occurs at the top of the bed. A radiant waste heat boiler is used at the top of the generator to cool the gas and thus prevent blockage of exit ports by buildup of molten ash particles.

The Winkler generator can gasify coal tars, heavy fuel oils, and a variety of coals, although some are more desirable than others, Caking coals, as a rule, cannot be gasified in fluid-bed systems without pretreatment to render them noncaking. Processing of coals of low reactivity requires higher operating temperatures to assure high char utilization. Coals with high ash content can be processed in the Winkler generator. In respect to turndown and capacity, a generator with a nominal capacity of 2 x 10^6 scfh can be operated in the range of 500,000 to 3 x 10^6 scfh. Total shutdown can be achieved in minutes simply by shutdown of all feed streams. The heat content in the generator fuel bed is sufficient to allow startup by reintroduction of oxygen and steam even after several days. Heat loss during shutdown can be compensated by injection of air into the fuel bed once or twice daily. On-stream availability of 91 percent is claimed.

Of over 30 Winkler generators built since 1926, six are presently operating: two in Kutahya, Turkey, three in Madras, India, and one in Gorazde, Yugoslavia.

TABLE C-3. TYPICAL WINKLER PRODUCER GAS COMPOSITIONS

Plant Location	Gorazde, Yugoslavia	Kutahya, Turkey	Wesseling, Germany	Toyo-Koatsu, Japan
Plant Number	10	14	16	8
Year Built	1953	1959	1960	1939
Product	Synthesis gas	Synthesis gas	Synthesis gas	Synthesis gas
Current Status	Operating	Operating	Unknown	Unknown
Feed Coal Type	Subbituminous	Lignite	Lignite	Moderately caking bituminous
Ash, percent weight	24	27	4	
Water, percent weight	3	3	9	
Volatiles, percent weight	39	37	47	
Gas Composition, volume percent				
CO	37	35	48.2	34
H_2	37	40	35.3	31
CO_2	20	20	13.8	12
CH_4	3	3	1.8	0.5
N_2	3	2	0.9	22.5
HHV, dry				
Btu/scf	269	272	287	215

The Riley-Morgan Gasifier(3)

The Riley-Morgan gasifier is a modified version of the Morgan gasifier. About 3000 units of this gasifier were used in the U.S. before 1940. With the advent of natural gas these were abandoned. Thus, the Riley-Morgan gasifier can be considered commercially demonstrated.

The Riley gasifier can be either air blown or oxygen blown. The gas at the exit of the gasifier is at 650 C (1200 F) and a pressure of +35 in water gauge.

The gasifier is of conventional fixed-bed design with a 10-1/2-foot diameter chamber. The outer shell of the unit rotates while the grate on the inside of the unit remains stationary. This rotating action helps to break up the fuel bed and prevent clinkering tendency of caking coals. Riley Stoker Company has been operating a 10-1/2 foot commercial size unit at their Worcester, Massachusetts, facilities since June, 1975; prior to which a pilot plant was in operation. Trace elements data appear to have been collected at their facilities in response to requests from clients who are vendors of sulfur-producing FGD processes, but Riley is not willing to publish such data for proprietary reasons.

A detailed flow diagram of the Riley coal gasification system for medium-Btu gas generation is shown in Figure C-4. Gas composition for air and oxygen operations with Ohio bituminous coal are presented in Table C-4.

Reported oxygen consumption in the Riley system is 0.93 lb per pound of fixed carbon in the coal. On this basis, for the coal in Table C-4, the oxygen consumption is 0.4 lb per lb of coal. Since this coal can be considered typical, the oxygen/coal ratio of 0.4 is much lower than the average value of 0.7 for the other gasifiers discussed. Because the Riley oxygen requirement is not a published value, but was obtained during telephone communication with Riley personnel, a closer evaluation of the oxygen/coal ratio may be necessary at a later stage.

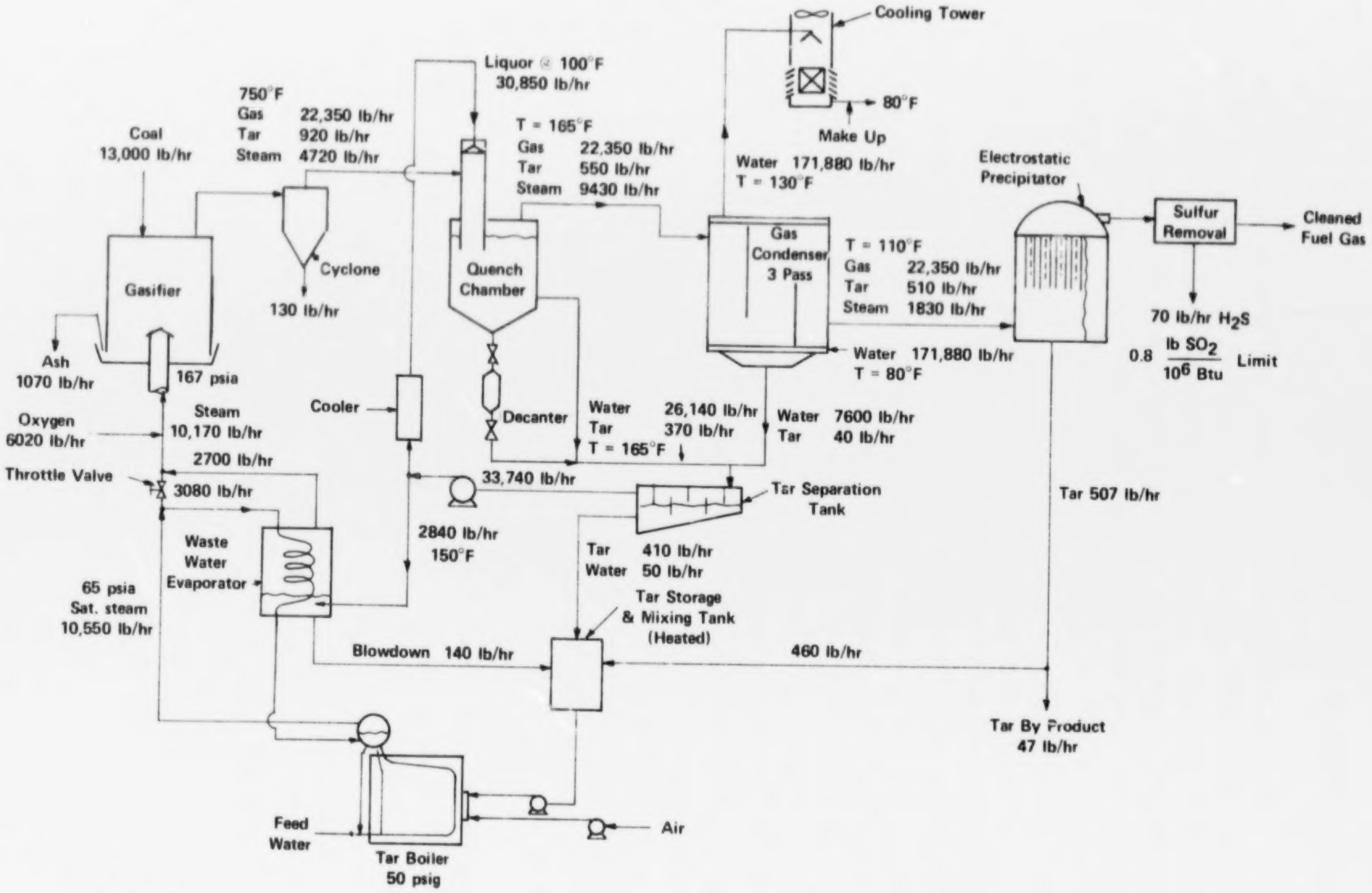
Coal
13,000 lb/hr
Gasifier
Ash
1070 lb/hr
167 psia
Oxygen
6020 lb/hr
Steam
10,170 lb/hr
2700 lb/hr
Throttle Valve
3080 lb/hr
65 psia
Sat. steam
10,550 lb/hr
750°F
Gas 22,350 lb/hr
Tar 920 lb/hr
Steam 4720 lb/hr
Cyclone
130 lb/hr
Cooler
Waste
Water
Evaporator
2840 lb/hr
150°F
33,740 lb/hr
Liquor @ 100°F
30,850 lb/hr
T = 165°F
Gas 22,350 lb/hr
Tar 550 lb/hr
Steam 9430 lb/hr
Quench
Chamber
Decanter
Water 26,140 lb/hr
Tar 370 lb/hr
T = 165°F
Cooling Tower
80°F
Make Up
Water 171,880 lb/hr
T = 130°F
Gas
Condenser
3 Pass
T = 110°F
Gas 22,350 lb/hr
Tar 510 lb/hr
Steam 1830 lb/hr
Water 171,880 lb/hr
T = 80°F
Water 7600 lb/hr
Tar 40 lb/hr
Tar Separation
Tank
Tar 410 lb/hr
Water 50 lb/hr
Tar Storage
& Mixing Tank
(Heated)
Blowdown 140 lb/hr
460 lb/hr
Electrostatic
Precipitator
Sulfur
Removal
Cleaned
Fuel Gas
70 lb/hr H2S
0.8 lb SO2 / 10^6 Btu Limit
Tar 507 lb/hr
Tar By Product
47 lb/hr
Feed
Water
Tar Boiler
50 psig
Air

FIGURE C-4. FLOW DIAGRAM OF THE RILEY-MORGAN INTERMEDIATE-BTU COAL GASIFICATION SYSTEM

TABLE C-4. TYPICAL ANALYSES OF FUEL GAS FROM RILEY-MORGAN GASIFIER

	Air-Steam Operation	Oxygen-Steam Operation
Coal Type	Ohio bituminous	Ohio bituminous
Coal Assay, percent		
Moisture	7.2	7.2
Volatiles	34.4	34.4
Fixed carbon	42.7	42.7
Ash	15.7	15.7
Heating value, Btu/lb	11,315	11,315
Gas Assay		
CO	26.0	41.2
H_2	18.4	38.9
CO_2	3.8	15.9
CH_4	1.6	2.8
CH_4+	0.2	0.7
N_2 + Ar	50.0	0.5
HHV	163.0	305
Sp. gravity	0.82	0.70

Source: Telephone communications with Thomas F. Walsh, Sales Manager, Riley Stoker Corp., Worcester, Mass.

Summary of Coal Gasifier Characteristics

While the K-T gasifier can be operated only on oxygen, the others can use either air or oxygen. Due to very high temperature operation, the K-T does not produce ammonia or methane in any significant quantities, but the gas contains up to 50 percent of the ash in the coal as fly ash. The K-T has the lowest overall thermal efficiency (67 percent) of the four gasifiers, whereas the Wellman-Galusha has the highest efficiency (82 percent). The turndown capability of the K-T is lower than that of the other three gasifiers.

The K-T gasifier, being a suspension type, has the highest rate of gasification (pounds of coal gasified per hour per unit volume of reactor). Thus, K-T will offer a smaller sized unit.

Residual Oil Gasification Processes

Two commercially proven heavy oil gasifiers are: (1) the Shell Gasification process and (2) the Texaco partial oxidation process. More than 100 Shell gasification reactors with >95 percent on-stream availability and about 60 Texaco gasification plants are in commercial use.

Shell Gasification Process(6,7)

In the Shell process, any hydrocarbon feedstock can be converted into gas by controlled partial oxidation in a special noncatalytic reactor. A generalized flow diagram of the process is presented in Figure C-5. The heavy oil feed, mixed with recycled carbon in a homogenizer, is heated and fed to the reactor along with oxygen and steam. Air can be used instead of oxygen. In the reactor, partial combustion of the feed provides the energy for cracking and gasification at temperatures of 1000 to 1600 C (1800 to 2900 F). The waste heat boiler producing high pressure steam is said to be extremely compact due to prevailing high heat transfer rates.

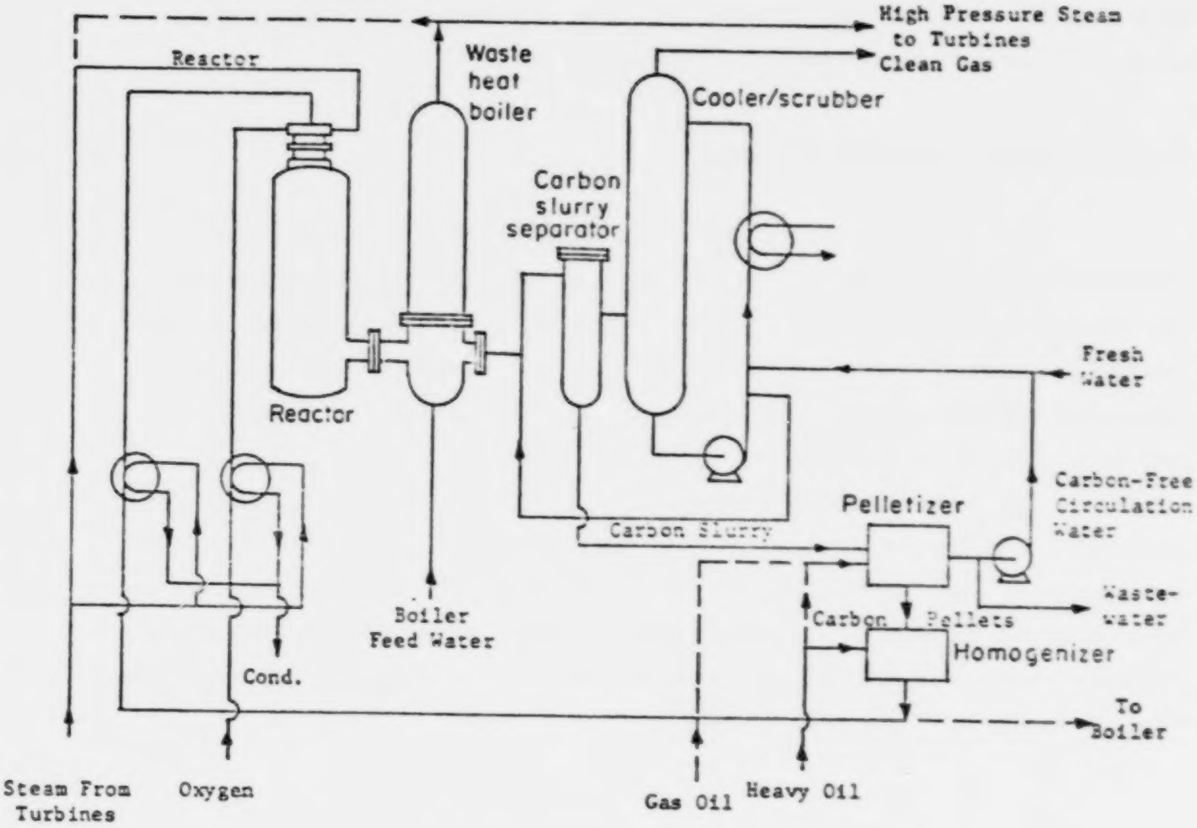
High Pressure Steam to Turbines
Clean Gas
Reactor
Waste heat boiler
Cooler/scrubber
Carbon slurry separator
Fresh Water
Reactor
Carbon-Free Circulation Water
Pelletizer
Carbon Slurry
Waste-water
Carbon
Pellets
Homogenizer
Boiler Feed Water
Cond.
To Boiler
Steam From Turbines
Oxygen
Gas Oil
Heavy Oil

FIGURE C-5. GENERALIZED SCHEMATIC DIAGRAM OF THE SHELL GASIFICATION PROCESS

Source: Reference 7.

Most of the carbon for recycle to the process is recovered in the gas purification section. The gas is virtually carbon-free (less than 4 ppm). Typical gas compositions for air-steam and oxygen-steam modes of reactor operation are provided in Table C-6.

Texaco Partial Oxidation Process(8)

The Texaco process, also called the Texaco Synthesis Gas Generation Process (TSGGP), is used in over 20 countries on a variety of feedstocks, primarily heavy oils. One of these installations at the Texaco Refinery in Los Angeles has met all the stringent air and water pollution control regulations. Eventually, the process is expected to use coal also as a feedstock.

The TSGGP employs a noncatalytic flame reaction in an oxygen deficient atmosphere to produce hydrogen and carbon monoxide. Reactor temperatures range from 1100 to 1600 C (2000 to 2800 F) and pressures from nearly 1 to over 136 atmospheres. A typical gas composition from a straight residue feedstock is shown in Table C-7. A general process flow diagram is provided in Figure C-6.

TABLE C-6. TYPICAL GAS COMPOSITION FROM SHELL GASIFICATION PROCESS

(Dry Basis)

	Feedstock			
	Heavy Fuel Oil	Propane Asphalt	Vacuum Residuum	
Oxidizing Medium	Oxygen	Oyxgen	Oxygen	Air
Composition, volume percent				
H_2	46.7	44.2	47.1	14.5
CO	46.2	47.8	50.8	23.6
CO_2	4.3	4.5	1.2	1.0
CH_4	0.6	0.6	0.6	0.2
N_2 + argon	1.4	1.3	1.2	60.7
H_2S and COS(a)	0.8	1.6	0.04	0.02

(a) Depends on feed sulfur content.

Sources: (1) Hydrocarbon Processing, April, 1975, p 117.
(2) Reference 6.

TABLE C-7. TYPICAL SYNTHESIS GAS COMPOSITION FROM TEXACO GASIFIER

Feed	Straight petroleum residue
Oxidizing Medium	Oxygen/steam
Product Gas Composition, volume percent	
CO	47.0
H_2	47.0
CO_2	5.6
N_2 + A	0.2
CH_4	0.1
H_2S(a)	0.1

(a) Proportional to feed sulfur content.

Source: Telephone communications with Dr. Edward T. Childs, Texaco Development Corporation, New York, New York, (212) 953-6000.

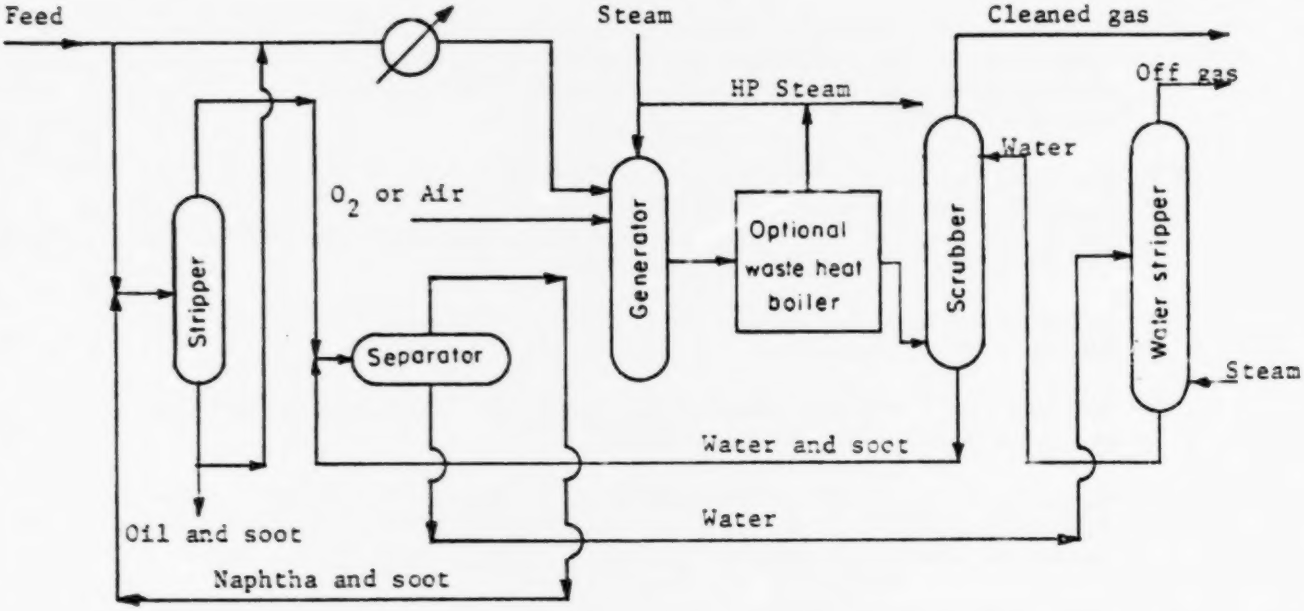
Feed
Steam
Cleaned gas
HP Steam
Off gas
Water
O_2 or Air
Stripper
Separator
Generator
Optional waste heat boiler
Scrubber
Water stripper
Steam
Water and soot
Oil and soot
Water
Naphtha and soot

FIGURE C-6. SCHEMATIC DIAGRAM OF THE TEXACO GASIFICATION PROCESS

Source: Hydrocarbon Processing, April, 1975, p 133.

REFERENCES

(1) Mudge, L. K., et al, "The Gasification of Coal", A Battelle Energy Program Report, Battelle Memorial Institute, Columbus, Ohio, July, 1974.

(2) Mitsak, D. M., "Koppers-Totzek: Take a Long Hard Look", 2nd Annual Symposium on Coal Gasification, Liquefaction, and Utilization: Best Prospects for Commercialization, University of Pittsburgh, August 5-7, 1975.

(3) Cobb, R. W., et al, "Analysis of a Coal Gasification Facility and Potential Gas Using Industries for Pike County, Kentucky", BCL report to Appalachian Regional Commission, Commonwealth of Kentucky, and Pike County Fiscal Court, September 1, 1975.

(4) McDowell Wellman Engineering Co., "Wellman-Galusha Gas Producers", brochure (Form No. 576).

(5) Banchik, I. N., "The Winkler Process for the Production of Low-Btu Gas from Coal", Day Powergas, Inc.

(6) Plummer, J. B., et al, "The Generation of Clean Gaseous Fuels from Petroleum Residues", presented by Shell Development Company, Houston, Texas, at the AIChE meeting, Tulsa, Oklahoma, March 11-13, 1974.

(7) Shell Development Company, "The Shell Gasification Process" brochure.

(8) Child, E. T., "Texaco: Heavy Oil Gasification", Symposium on Coal Gasification and Liquefaction: Best Prospects for Commercialization, University of Pittsburgh, August 6-8, 1974.

APPENDIX D

CALCULATION OF TRACE CONSTITUENT DISTRIBUTIONS

APPENDIX D

CALCULATION OF TRACE CONSTITUENT DISTRIBUTIONS

This appendix presents additional details related to the computer calculation of trace constituent distributions for gasification processes. The first section includes a comparison of the computer program used in this study with other similar programs. The second section presents the detailed computer output data, i.e., the predicted equilibrium compositions of the gaseous and solid phases.

Comparison of Equilibrium Calculation Computer Programs

The technique employed to compute thermodynamic equilibrium values in this study was based on the EQUICA program developed by Battelle based on the work of Cruise.(1) Other programs available for computing equilibrium calculations include the NASA program, which utilizes the free energy minimization method, and the Naval Ordinance Test Station (NOTS) program.(2) In a recent Battelle study for the U.S. Coast Guard, these programs were evaluated for relative accuracy.(3) A brief summary of the results of the study is presented in Tables D-1 and D-2. Accordingly, the difference between estimating accuracy of NASA and EQUICA is negligible. However, the NASA program uses more automatic computing processes and therefore can be less expensive in computing time cost when very large calculations are involved.

Computer Output Data on Trace Constituents

This section contains the computer printouts giving the detailed trace constituent distributions. The following tables are included:

TABLE D-1. COMPARISON OF EQUILIBRIUM COMPOSITIONS CALCULATED

(Thermal Decomposition of Acrylonitrite at
1300 K and 1 atm Pressure)

Species	EQUICA	NASA
HCN	3.459×10^{-5}	3.5258×10^{-5}
NH_3	1.746×10^{-5}	1.6047×10^{-5}
C(S)	6.004×10^{-1}	6.0034×10^{-1}
H_2	2.970×10^{-1}	2.9756×10^{-1}
N_2	1.004×10^{-1}	1.0032×10^{-1}
CH_4	2.121×10^{-3}	1.7257×10^{-3}
H	4.503×10^{-7}	3.7969×10^{-7}
C_2H_2	1.789×10^{-7}	2.0284×10^{-7}
CH_3	4.831×10^{-8}	5.1507×10^{-8}
H_2N	2.699×10^{-10}	3.0380×10^{-10}

Source: Reference 3.

TABLE D-2. COMPARISON OF DECOMPOSITION TEMPERATURES CALCULATED BY PROGRAMS NOTS AND NASA

	Decomposition Temperature, K	
	NOTS	NASA
Nitroethane	1161	1161
Epichlorohydrin	1042	1042
Acrylonitrile	1896	1891
Nitrobenzene	1540	1538
Acetic acid	652	655
Butyraldehyde	800	801
Propylene oxide	951	951
Acetylene + O_2	3341 (To)	3341 (To)

Table Number	System	Temperature, C (F)
D-3	Power plant boiler	650 (1200)
D-4	Koppers-Totzek gasifier	1815 (3300)
D-5	Koppers-Totzek gasifier	650 (1200)
D-6	Winkler gasifier	980 (1800)
D-7	Wellman-Galusha gasifier	650 (1200)
D-8	Riley-Morgan gasifier	680 (1250)

TABLE D-3. TRACE ELEMENTS DISTRIBUTION IN BOILER AT 1200 F

(98 PERCENT BY WEIGHT OF THE FOLLOWING CONDENSED SPECIES ARE INCLUDED
IN THE PRODUCT GAS STREAM AS FLY ASH; THE BALANCE IS REMOVED AS ASH)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)	PPM BY WT. (IN ASH)
SIO2	60.1	.75779E-02	.45543E+00	.4159038	4159.038	4200.723	542290.008
CAO	56.1	.14730E-02	.82633E-01	.0754615	754.615	762.178	98392.938
FE3O4	231.6	.97950E-03	.22685E+00	.2071634	2071.634	2092.397	270116.866
MGO	40.3	.17578E-03	.70839E-02	.0064691	64.691	65.339	8434.955
K2O	94.2	.17391E-03	.16382E-01	.0149603	149.603	151.103	19506.505
CACL2	111.0	.16797E-03	.18645E-01	.0170268	170.268	171.975	22201.001
TIO2	79.9	.12299E-03	.98269E-02	.0089740	89.740	90.639	11701.050
NA2CO3	106.0	.92581E-04	.98136E-02	.0089618	89.618	90.517	11685.202
AL2O3	101.9	.43264E-04	.44086E-02	.0040260	40.260	40.663	5249.394
B2O3	69.6	.39751E-04	.27667E-02	.0025266	25.266	25.519	3294.340
ZNO	81.4	.35580E-04	.28969E-02	.0026455	26.455	26.720	3449.439
MNO	70.9	.67268E-05	.47693E-03	.0004355	4.355	4.399	567.888
ZRO2	123.2	.50938E-05	.62756E-03	.0005731	5.731	5.788	747.241
NIO	74.7	.23013E-05	.17191E-03	.0001570	1.570	1.586	204.693
V2O4	165.9	.20584E-05	.34149E-03	.0003118	3.118	3.150	406.616
CUO	79.5	.14025E-05	.11150E-03	.0001018	1.018	1.028	132.763
PBO	223.2	.11473E-05	.25608E-03	.0002339	2.339	2.362	304.919
TIN	61.9	.97610E-06	.60421E-04	.0000552	.552	.557	71.944
TI	47.9	.97609E-06	.46755E-04	.0000427	.427	.431	55.672
MN	54.9	.96095E-06	.52756E-04	.0000482	.482	.487	62.818
C	12.0	.94450E-06	.11334E-04	.0000104	.104	.105	13.496
SI	28.1	.92515E-06	.25997E-04	.0000237	.237	.240	30.955
ZRN	105.2	.84894E-06	.89313E-04	.0000816	.816	.824	106.346
ZR	91.2	.84893E-06	.77422E-04	.0000707	.707	.714	92.188
K	39.1	.79308E-06	.31010E-04	.0000283	.283	.286	36.924
NI	58.7	.76708E-06	.45028E-04	.0000411	.411	.415	53.615
BEO	25.0	.76410E-06	.19102E-04	.0000174	.174	.176	22.746
CAS	72.2	.76080E-06	.54930E-04	.0000502	.502	.507	65.406
CA	40.1	.76080E-06	.30508E-04	.0000279	.279	.281	36.326
FE	55.9	.71758E-06	.40113E-04	.0000366	.366	.370	47.763
AL	27.0	.68672E-06	.18541E-04	.0000169	.169	.171	22.078
ALN	41.0	.68672E-06	.28156E-04	.0000257	.257	.260	33.525
VN	65.0	.68616E-06	.44600E-04	.0000407	.407	.411	53.106
V	51.0	.68606E-06	.34989E-04	.0000320	.320	.323	41.662
CR2O3	152.0	.67172E-06	.10210E-03	.0000932	.932	.942	121.574
NAOH	40.0	.65258E-06	.26103E-04	.0000238	.238	.241	31.082
CU	63.5	.63750E-06	.40481E-04	.0000370	.370	.373	48.202
BN	24.8	.63097E-06	.15648E-04	.0000143	.143	.144	18.632
B	10.8	.63097E-06	.68145E-05	.0000062	.062	.063	8.114
CR	52.0	.56433E-06	.29345E-04	.0000268	.268	.271	34.942
BE	9.0	.38195E-06	.34376E-05	.0000031	.031	.032	4.093
CRCL2	122.9	.35193E-06	.43252E-04	.0000395	.395	.399	51.501
CDCL2	183.3	.18847E-06	.34547E-04	.0000315	.315	.319	41.135
PB	207.2	.17939E-06	.37170E-04	.0000339	.339	.343	44.258
BE3N2	55.1	.12742E-06	.70208E-05	.0000064	.064	.065	8.360
NA	23.0	.12195E-06	.28049E-05	.0000026	.026	.026	3.340
PBCL2	278.1	.10869E-06	.30227E-04	.0000276	.276	.279	35.991
SB2O3	291.5	.33204E-07	.96790E-05	.0000088	.088	.089	11.525

TABLE D-3. (Continued)

SB	121.8	.13292E-07	.23498E-05	.0000021	.021	.022	2.798
ZN	65.4	.17603E-07	.11512E-05	.0000011	.011	.011	1.371
CDO	128.4	.34211E-08	.43927E-06	.0000004	.004	.004	.523
CR3C2	181.1	.40000E-09	.73240E-07	.0000001	.001	.001	.087
CAC2	64.1	.20000E-09	.12820E-07	.0000000	.000	.000	.015
SIC	40.1	.20000E-09	.80200E-08	.0000000	.000	.000	.010
VC	63.0	.20000E-09	.12600E-07	.0000000	.000	.000	.015
TIC	59.9	.20000E-09	.11980E-07	.0000000	.000	.000	.014
NA2O	62.0	.10000E-09	.62000E-08	.0000000	.000	.000	.007
HG	200.6	.10000E-09	.20060E-07	.0000000	.000	.000	.024
MG	24.3	.39990E-10	.97176E-09	.0000000	.000	.000	.001
CD	112.4	.62361E-11	.70094E-09	.0000000	.000	.000	.001
MGCL2	95.2	.0	.0	0.0000000	0.000	0.000	0.000

						TOTAL	1000000.00

(THE FOLLOWING GASEOUS SPECIES WERE PREDICTED)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)
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N2	28.0	.27375E+01	.76650E+02	70.7044055	707044.055	706989.285
CO2	44.0	.50022E+00	.22010E+02	20.3024392	203024.392	203008.665
H2O	18.0	.22759E+00	.40966E+01	3.7788537	37788.537	37765.610
O2	32.0	.11757E+00	.37621E+01	3.4702989	34702.989	34700.300
SO2	64.1	.16499E-01	.10576E+01	.9755510	9755.510	9754.754
P4O10	283.9	.49056E-05	.13927E-02	.0012847	12.847	12.846
K	39.1	.11303E-05	.44194E-04	.0000408	.408	.408
AS2O3	197.8	.80015E-06	.15827E-03	.0001460	1.460	1.460
SEO2	111.0	.22518E-06	.24995E-04	.0000231	.231	.231
CL2	70.9	.14989E-06	.10627E-04	.0000098	.098	.098
KO	55.1	.11834E-06	.65207E-05	.0000060	.060	.060
HGO	216.6	.62189E-08	.13470E-05	.0000012	.012	.012
HG	200.6	.22461E-08	.45056E-06	.0000004	.004	.004
HGCL2	271.5	.23517E-09	.63850E-07	.0000001	.001	.001
SEO	95.0	.20075E-09	.19071E-07	.0000000	.000	.000
SE	79.0	.14100E-10	.11139E-08	.0000000	.000	.000
CO	28.0	.11577E-10	.32415E-09	.0000000	.000	.000
PB	207.2	.93854E-11	.19447E-08	.0000000	.000	.000
H2	2.0	.90916E-11	.18183E-10	.0000000	.000	.000
BO2	42.8	.16351E-11	.69984E-10	.0000000	.000	.000
FE(OH)2	89.9	.27295E-12	.24538E-10	.0000000	.000	.000
NA	23.0	.10341E-12	.23784E-11	.0000000	.000	.000
BECL2	79.9	.64143E-13	.51250E-11	.0000000	.000	.000
AS	74.9	.79222E-14	.59337E-12	.0000000	.000	.000
ALCL3	133.3	.67457E-18	.89921E-16	.0000000	.000	.000
TICL4	189.7	.76001E-19	.14417E-16	.0000000	.000	.000
NH3	17.0	.10440E-19	.17749E-18	.0000000	.000	.000
BO	26.8	.73592E-23	.19723E-21	.0000000	.000	.000
ZRCL4	233.1	.79924E-24	.18631E-21	.0000000	.000	.000
S	32.1	.21814E-25	.70024E-24	.0000000	.000	.000
H2S	34.1	.13174E-25	.44922E-24	.0000000	.000	.000
COS	60.1	.63436E-27	.38125E-25	.0000000	.000	.000
CA(OH)2	74.1	.72275E-28	.53556E-26	.0000000	.000	.000
FE	55.9	.77265E-29	.43191E-27	.0000000	.000	.000
ALOH	44.0	.48143E-33	.21183E-31	.0000000	.000	.000

TABLE D-3. (Continued)

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P                    31.0    .65849E-40    .20413E-38    .0000000          .000          .000
CH4                  16.0    .99025E-45    .15844E-43    .0000000          .000          .000
CS2                  76.1    .26998E-54    .20546E-52    .0000000          .000          .000
SI                   28.1    .60100E-57    .16888E-55    .0000000          .000          .000
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      TOTALS                               .10841E+03    100.000000    1000000.00    1000000.00
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TABLE D-4. TRACE ELEMENT DISTRIBUTION IN K-T COAL GASIFIER AT 3300 F

(50 PERCENT BY WEIGHT OF THE FOLLOWING CONDENSED SPECIES ARE INCLUDED IN THE PRODUCT GAS STREAM AS FLY ASH; THE BALANCE IS REMOVED AS ASH)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)	PPM BY WT. (IN ASH)
SIO2	60.1	.75764E-02	.45534E+00	1.4616473	14616.473	28583.901	643708.682
FE	55.9	.21657E-02	.12106E+00	.3886140	3886.140	7599.716	171145.406
CAS	72.2	.16397E-02	.11839E+00	.3800256	3800.256	7431.761	167363.057
TIO2	79.9	.12268E-03	.98018E-02	.0314635	314.635	615.299	13856.520
MNO	70.9	.71472E-05	.50673E-03	.0016206	16.206	31.810	716.356
ZRO2	123.2	.50938E-05	.62755E-03	.0020144	20.144	39.394	887.158
NI	58.7	.24931E-05	.14634E-03	.0004698	4.698	9.187	206.862
V2O4	165.9	.18761E-05	.31124E-03	.0009991	9.991	19.538	439.990
TI	47.9	.97609E-06	.46755E-04	.0001501	1.501	2.935	66.096
AL	27.0	.95118E-06	.25682E-04	.0000824	.824	1.612	36.306
NA2CO3	106.0	.94562E-06	.10024E-03	.0003218	3.218	6.292	141.700
CAO	56.1	.87457E-06	.49063E-04	.0001575	1.575	3.080	69.359
SIC	40.1	.86732E-06	.34780E-04	.0001116	1.116	2.183	49.167
ZRN	105.2	.84897E-06	.89311E-04	.0002867	2.867	5.606	126.257
ZR	91.2	.84893E-06	.77422E-04	.0002485	2.485	4.860	109.449
B2O3	69.6	.79274E-06	.55175E-04	.0001771	1.771	3.464	77.999
ALN	41.0	.77777E-06	.31888E-04	.0001024	1.024	2.002	45.080
CAC2	64.1	.76671E-06	.49146E-04	.0001578	1.578	3.085	69.477
TIC	59.9	.70157E-06	.42024E-04	.0001349	1.349	2.638	59.409
CACL2	111.0	.67502E-06	.74927E-04	.0002405	2.405	4.703	105.922
C	12.0	.65987E-06	.79185E-05	.0000254	.254	.497	11.194
MGO	40.3	.64719E-06	.26082E-04	.0000837	.837	1.637	36.871
B	10.8	.60345E-06	.65173E-05	.0000209	.209	.409	9.213
VC	63.0	.60075E-06	.37847E-04	.0001215	1.215	2.376	53.504
VN	65.0	.60040E-06	.39026E-04	.0001253	1.253	2.450	55.170
SI	28.1	.59990E-06	.16857E-04	.0000541	.541	1.058	23.831
FE3O4	231.6	.59158E-06	.13701E-03	.0004398	4.398	8.601	193.687
TIN	61.9	.58718E-06	.36347E-04	.0001167	1.167	2.282	51.382
BN	24.8	.57778E-06	.14329E-04	.0000450	.450	.899	20.256
NIO	74.7	.57533E-06	.42977E-04	.0001380	1.380	2.698	60.756
AL2O3	101.9	.54802E-06	.55843E-04	.0001793	1.793	3.505	78.944
MN	54.9	.54054E-06	.29676E-04	.0000953	.953	1.863	41.952
V	51.0	.53602E-06	.27337E-04	.0000878	.878	1.716	38.646
BEO	25.0	.36297E-06	.90742E-05	.0000291	.291	.570	12.828
CR2O3	152.0	.77625E-07	.11799E-04	.0000379	.379	.741	16.680
CR3C2	180.1	.47193E-07	.85419E-05	.0000277	.277	.542	12.217
BE3N2	55.1	.31935E-07	.17596E-05	.0000056	.056	.110	2.488
K2O	94.2	.10000E-09	.94200E-08	.0000000	.000	.001	.013
NA	23.0	.10000E-09	.23000E-08	.0000000	.000	.000	.003
AS2O3	197.8	.10000E-09	.19780E-07	.0000001	.001	.001	.028
ZNO	81.4	.10000E-09	.81400E-08	.0000000	.000	.001	.012
NA2O	62.0	.10000E-09	.62000E-08	.0000000	.000	.000	.009
CUO	79.5	.10000E-09	.79500E-08	.0000000	.000	.000	.011
K	39.1	.10000E-09	.39100E-08	.0000000	.000	.000	.006
HG	200.6	.10000E-09	.20060E-07	.0000001	.001	.001	.028
						TOTAL	1000000.00

TABLE D-4. (Continued)

(THE FOLLOWING GASEOUS SPECIES WERE PREDICTED)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)
CO	28.0	.49770E+00	.13936E+02	89.4662801	894662.801	874799.038
H2	2.0	.31644E+00	.63289E+00	4.0631276	40631.275	39729.160
H2S	34.1	.65285E-02	.22262E+00	1.4292163	14292.163	13974.841
H2O	18.0	.60358E-02	.10864E+00	.6974968	6974.958	6820.106
N2	28.0	.39647E-02	.11101E+00	.7126922	7126.922	6968.686
CO2	44.0	.22367E-02	.98413E-01	.6318097	6318.097	6177.819
FE	55.9	.77157E-03	.43131E-01	.2768987	2768.987	2707.509
COS	60.1	.35205E-03	.21158E-01	.1358343	1358.343	1328.185
K	39.1	.34986E-03	.13680E-01	.0878220	878.220	858.721
NA	23.0	.18301E-03	.42091E-02	.0270225	270.225	264.226
S	32.1	.17711E-03	.56851E-02	.0364981	364.981	356.878
MG	24.3	.13563E-03	.32957E-02	.0211585	211.585	206.887
ALCL3	133.3	.85055E-04	.11338E-01	.0727893	727.893	711.732
BO	26.8	.76150E-04	.20408E-02	.0131019	131.019	128.110
MGCL2	95.2	.39506E-04	.37610E-02	.0241453	241.453	236.092
ZN	65.4	.35607E-04	.23287E-02	.0149503	149.503	146.184
P	31.0	.19622E-04	.60829E-03	.0039052	39.052	38.185
CS2	76.1	.16612E-04	.12642E-02	.0081161	81.161	79.359
CU	63.5	.20399E-05	.12953E-03	.0008316	8.316	8.131
CR	52.0	.19566E-05	.10174E-03	.0006532	6.532	6.387
BO2	42.8	.18482E-05	.79101E-04	.0005078	5.078	4.966
AS	74.9	.16001E-05	.11985E-03	.0007694	7.694	7.523
NAOH	40.0	.10430E-05	.41720E-04	.0002678	2.678	2.619
BECL2	79.9	.99704E-06	.79664E-04	.0005114	5.114	5.001
SI	28.1	.87863E-06	.24689E-04	.0001585	1.585	1.550
PB	207.2	.71755E-06	.14868E-03	.0009545	9.545	9.333
PB	207.2	.71755E-06	.14868E-03	.0009545	9.545	9.333
SO2	64.1	.71683E-06	.45953E-04	.0002950	2.950	2.885
CA	40.1	.45190E-06	.18121E-04	.0001163	1.163	1.138
SE	79.0	.22536E-06	.17803E-04	.0001143	1.143	1.118
CD	112.4	.19190E-06	.21569E-04	.0001385	1.385	1.354
FE(OH)2	89.9	.13534E-06	.12167E-04	.0000781	.781	.764
NH3	17.0	.12745E-06	.21666E-05	.0000139	.139	.136
CH4	16.0	.86146E-07	.13783E-05	.0000088	.088	.087
SB	121.8	.85700E-07	.10438E-04	.0000670	.670	.655
BE	9.0	.72484E-07	.65236E-06	.0000042	.042	.041
ALOH	44.0	.19577E-07	.86137E-06	.0000055	.055	.054
HG	200.6	.86997E-08	.17452E-05	.0000112	.112	.110
CRCL2	122.9	.74543E-08	.91613E-06	.0000059	.059	.058
CL2	70.9	.16773E-08	.11892E-06	.0000008	.008	.007
KO	55.1	.55415E-09	.30534E-07	.0000002	.002	.002
PBO	223.2	.22779E-09	.50843E-07	.0000003	.003	.003
O2	32.0	.98931E-10	.31658E-08	.0000000	.000	.000
PBCL2	278.1	.73661E-10	.20485E-07	.0000001	.001	.001
SEO	95.0	.44186E-10	.41977E-08	.0000000	.000	.000
ZRCL4	233.1	.20644E-10	.48129E-08	.0000000	.000	.000
TICL4	189.7	.20648E-10	.39168E-08	.0000000	.000	.000
CA(OH)2	74.1	.71243E-11	.52791E-09	.0000000	.000	.000
P4O10	283.9	.41061E-11	.11657E-08	.0000000	.000	.000
COCL2	183.3	.17705E-11	.32454E-09	.0000000	.000	.000
HGO	216.6	.31585E-12	.68414E-10	.0000000	.000	.000

TABLE D-4. (Continued)

COO	128.4	.16873E-13	.21665E-11	.0000000	.000	.000
HGCL2	271.5	.15277E-15	.41478E-13	.0000000	.000	.000
SEO2	111.0	.16487E-16	.18301E-14	.0000000	.000	.000
SB203	291.5	.52085E-25	.15183E-22	.0000000	.000	.000
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TOTALS		0.817305	.15576E+02	100.000000	1000000.00	1000000.00

TABLE D-5. TRACE ELEMENT DISTRIBUTION IN K-T COAL GASIFIER AT 1200 F

(0 PERCENT BY WEIGHT OF THE FOLLOWING CONDENSED SPECIES ARE INCLUDED
IN THE PRODUCT GAS STREAM AS FLY ASH; THE BALANCE IS REMOVED AS ASH)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)	PPM BY WT. (IN ASH)
NA2CO3	106.0	.90279E-04	.95695E-02	0.0000000	0.000	630.965	738452.392
ZNO	81.4	.35051E-04	.28531E-02	0.0000000	0.000	188.121	220167.773
PBCL2	278.1	.10757E-05	.29917E-03	0.0000000	0.000	19.725	23085.735
NA2O	62.0	.71649E-06	.44422E-04	0.0000000	0.000	2.929	3427.949
NA	23.0	.71648E-06	.16479E-04	0.0000000	0.000	1.087	1271.647
NAOH	40.0	.70161E-06	.28065E-04	0.0000000	0.000	1.850	2165.661
K	39.1	.68332E-06	.26718E-04	0.0000000	0.000	1.762	2061.737
ZN	65.4	.55636E-06	.36386E-04	0.0000000	0.000	2.399	2807.794
K2O	94.2	.51249E-06	.48277E-04	0.0000000	0.000	3.183	3725.366
CDCL2	183.3	.19162E-06	.35161E-04	0.0000000	0.000	2.318	2713.253
AL2O3	101.9	.52928E-08	.53934E-06	0.0000000	0.000	.036	41.619
TIO2	79.9	.31444E-08	.25124E-06	0.0000000	0.000	.017	19.387
ZRO2	123.2	.16222E-08	.19985E-06	0.0000000	0.000	.013	15.422
TIC	59.9	.87359E-09	.52328E-07	0.0000000	0.000	.003	4.038
TIN	61.9	.43680E-09	.27038E-07	0.0000000	0.000	.002	2.086
BEO	25.0	.43680E-09	.10920E-07	0.0000000	0.000	.001	.843
PB	207.2	.40000E-09	.82880E-07	0.0000000	0.000	.005	6.396
FE	55.9	.25863E-09	.14457E-07	0.0000000	0.000	.001	1.116
MGCL2	95.2	.20000E-09	.19040E-07	0.0000000	0.000	.001	1.469
CR2O3	152.0	.17500E-09	.26600E-07	0.0000000	0.000	.002	2.053
VC	63.0	.17500E-09	.11025E-07	0.0000000	0.000	.001	.851
FE3O4	231.6	.16854E-09	.39034E-07	0.0000000	0.000	.003	3.012
SIO2	60.1	.15000E-09	.90150E-08	0.0000000	0.000	.001	.696
NI	58.7	.15000E-09	.88050E-08	0.0000000	0.000	.001	.679
MNO	70.9	.15000E-09	.10635E-07	0.0000000	0.000	.001	.821
CACL2	111.0	.15000E-09	.16650E-07	0.0000000	0.000	.001	1.285
B2O3	69.6	.14408E-09	.10029E-07	0.0000000	0.000	.001	.774
BN	24.8	.12500E-09	.31000E-08	0.0000000	0.000	.000	.239
CAS	72.2	.12500E-09	.90250E-08	0.0000000	0.000	.001	.696
SIC	40.1	.12500E-09	.50125E-08	0.0000000	0.000	.000	.387
V	51.0	.10000E-09	.51000E-08	0.0000000	0.000	.000	.394
ALN	41.0	.10000E-09	.41000E-08	0.0000000	0.000	.000	.316
CU	63.5	.10000E-09	.63500E-08	0.0000000	0.000	.000	.490
C	12.0	.10000E-09	.12000E-08	0.0000000	0.000	.000	.093
TI	47.9	.10000E-09	.47900E-08	0.0000000	0.000	.000	.370
CA	40.1	.10000E-09	.40100E-08	0.0000000	0.000	.000	.309
PBO	223.2	.10000E-09	.22320E-07	0.0000000	0.000	.001	1.722
SB	121.8	.10000E-09	.12180E-07	0.0000000	0.000	.001	.940
CR	52.0	.10000E-09	.52000E-08	0.0000000	0.000	.000	.401
CRCL2	122.9	.10000E-09	.12290E-07	0.0000000	0.000	.001	.948
MGO	40.3	.10000E-09	.40300E-08	0.0000000	0.000	.000	.311
ZR	91.2	.10000E-09	.91200E-08	0.0000000	0.000	.001	.704
ZRN	105.2	.10000E-09	.10520E-07	0.0000000	0.000	.001	.812
AL	27.0	.10000E-09	.27000E-08	0.0000000	0.000	.000	.208
VN	65.0	.10000E-09	.65000E-08	0.0000000	0.000	.000	.502
SB2O3	291.5	.10000E-09	.29150E-07	0.0000000	0.000	.002	2.249
BE3N2	55.1	.10000E-09	.55100E-08	0.0000000	0.000	.000	.425
BE	9.0	.10000E-09	.90000E-09	0.0000000	0.000	.000	.069

TABLE D-5. (Continued)

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          CUO             79.5     .10000E-09    .79500E-08    0.0000000      0.000       .001       .613
          CAC2            64.1     .10000E-09    .64100E-08    0.0000000      0.000       .000       .495
          HG             200.6     .10000E-09    .20060E-07    0.0000000      0.000       .001      1.548
          CD             112.4     .84193E-10    .94640E-08    0.0000000      0.000       .001       .730
          V2O4           165.9     .62500E-10    .10369E-07    0.0000000      0.000       .001       .800
          NIO             74.7     .50000E-10    .37350E-08    0.0000000      0.000       .000       .288
          MN              54.9     .50000E-10    .27450E-08    0.0000000      0.000       .000       .212
          CR3C2          183.1     .50000E-10    .91550E-08    0.0000000      0.000       .001       .706
          SI              28.1     .25000E-10    .70250E-09    0.0000000      0.000       .000       .054
          CAO             56.1     .25000E-10    .14025E-08    0.0000000      0.000       .000       .108
          B               10.8     .48114E-11    .51963E-10    0.0000000      0.000       .000       .004
          CDO            128.4     .40508E-13    .52012E-11    0.0000000      0.000       .000       .000
          MG              24.3     .0            .0            0.0000000      0.000      0.000      0.000
                                                                                               ----------
                                                                                        TOTAL  1000000.00

                              (THE FOLLOWING GASEOUS SPECIES WERE PREDICTED)

          SPECIES       MOL. WT.       MOLES          GRAMS       WT. PERCENT   PPM BY WT.    PPM BY WT.
                                    (ASH+GAS)      (ASH+GAS)      (IN GAS)      (IN GAS)     (ASH+GAS)
          ----------   ----------   ----------     ----------    ----------    ----------    ----------
          CO                28.0    .36660E+00    .10265E+02    67.7384223    677384.223    676805.438
          H2                 2.0    .16469E+00    .32937E+00     2.1735592     21735.592     21717.020
          CH4               16.0    .70756E-01    .11321E+01     7.4708461     74708.461     74644.627
          CO2               44.0    .62303E-01    .27416E+01    18.0920852    180920.852    180766.265
          H2O               18.0    .16217E-01    .29190E+00     1.9262936     19262.936     19246.477
          H2S               34.1    .65822E-02    .22445E+00     1.4811914     14811.914     14799.258
          N2                28.0    .39620E-02    .11093E+00      .7320725      7320.725      7314.470
          COS               60.1    .55410E-03    .33301E-01      .2197607      2197.607      2195.729
          K                 39.1    .34815E-03    .13613E-01      .0898322       898.322       897.554
          ALCL3            133.3    .36927E-04    .49223E-02      .0324830       324.830       324.552
          TICL4            189.7    .24215E-04    .45936E-02      .0303134       303.134       302.875
          NH3               17.0    .50360E-05    .85612E-04      .0005650         5.650         5.645
          P4O10            283.9    .49054E-05    .13927E-02      .0091903        91.903        91.825
          CS2               76.1    .16539E-05    .12586E-03      .0008306         8.305         8.299
          AS                74.9    .16002E-05    .11985E-03      .0007909         7.909         7.903
          BECL2             79.9    .99670E-06    .79637E-04      .0005255         5.255         5.251
          ZRCL4            233.1    .71932E-06    .16767E-03      .0011065        11.065        11.055
          SE                79.0    .22540E-06    .17807E-04      .0001175         1.175         1.174
          NA                23.0    .12455E-07    .28647E-06      .0000019          .019          .019
          HG               200.6    .86846E-08    .17421E-05      .0000115          .115          .115
          CL2               70.9    .49051E-09    .34784E-07      .0000002          .002          .002
          PB               207.2    .31582E-09    .65439E-07      .0000004          .004          .004
          HGCL2            271.5    .15479E-10    .42027E-08      .0000000          .000          .000
          FE(OH)2           89.9    .13914E-10    .12509E-08      .0000000          .000          .000
          SO2               64.1    .13540E-11    .86793E-10      .0000000          .000          .000
          P                 31.0    .62307E-12    .19315E-10      .0000000          .000          .000
          S                 32.1    .11571E-12    .37142E-11      .0000000          .000          .000
          FE                55.9    .27021E-15    .15104E-13      .0000000          .000          .000
          KO                55.1    .14339E-15    .79008E-14      .0000000          .000          .000
          SEO               95.0    .12624E-16    .11992E-14      .0000000          .000          .000
          BO                26.8    .71350E-18    .19122E-16      .0000000          .000          .000
          BO2               42.8    .62355E-18    .25688E-16      .0000000          .000          .000
          HGO              216.6    .94584E-19    .20487E-16      .0000000          .000          .000
          ALOH              44.0    .14326E-22    .63036E-21      .0000000          .000          .000
          AS2O3            197.8    .10332E-22    .20437E-20      .0000000          .000          .000
```

TABLE D-5. (Continued)

```
     O2                     32.0    .34976E-24    .11192E-22     .0000000          .000          .000
     SE02                  111.0    .55694E-25    .61825E-23     .0000000          .000          .000
     SI                     28.1    .74688E-35    .20987E-33     .0000000          .000          .000
     CA(OH)2                74.1    .11900E-38    .88177E-37     .0000000          .000          .000
                                                  ----------   ----------    ----------    ----------
          TOTALS                                  .15154E+02   100.000000    1000000.00    1000000.00
```

TABLE D-6. TRACE ELEMENT DISTRIBUTION IN WINKLER GASIFIER AT 1800 F

(09 PERCENT BY WEIGHT OF THE FOLLOWING CONDENSED SPECIES ARE INCLUDED
IN THE PRODUCT GAS STREAM AS FLY ASH; THE BALANCE IS REMOVED AS ASH)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)	PPM BY WT. (IN ASH)
C	12.0	.17144E+00	.20573E+01	11.5678064	115678.064	154707.878	727241.004
SIO2	60.1	.75779E-02	.45543E+00	2.5607651	25607.651	34247.680	160989.326
FE	55.9	.29375E-02	.16421E+00	.9232988	9232.988	12348.201	58045.644
CAS	72.2	.14749E-02	.10649E+00	.5987585	5987.585	8007.799	37642.553
MGO	40.3	.17509E-03	.70563E-02	.0396756	396.756	530.622	2494.313
CACL2	111.0	.16617E-03	.18445E-01	.1037087	1037.087	1387.001	6519.926
TIO2	79.9	.12259E-03	.97950E-02	.0550745	550.745	736.567	3462.408
AL2O3	101.9	.43223E-04	.44044E-02	.0247650	247.650	331.208	1556.921
B2O3	69.6	.39751E-04	.27667E-02	.0155564	155.564	208.051	977.994
MNO	70.9	.67268E-05	.47693E-03	.0026816	26.816	35.864	168.588
ZRO2	123.2	.50935E-05	.62752E-03	.0035284	35.284	47.189	221.821
VC	63.0	.29163E-05	.18373E-03	.0010331	10.331	13.816	64.946
NI	58.7	.24931E-05	.14634E-03	.0008229	8.229	11.005	51.731
CU	63.5	.12750E-05	.80962E-04	.0004552	4.552	6.088	28.619
ZNO	81.4	.99588E-06	.81065E-04	.0004558	4.558	6.096	28.655
TIN	61.9	.97610E-06	.60420E-04	.0003397	3.397	4.544	21.358
TI	47.9	.97609E-06	.46755E-04	.0002629	2.629	3.516	16.527
MN	54.9	.96095E-06	.52756E-04	.0002966	2.966	3.967	18.649
SI	28.1	.92515E-06	.25997E-04	.0001462	1.462	1.955	9.190
ZRN	105.2	.84898E-06	.89312E-04	.0005022	5.022	6.716	31.571
ZR	91.2	.84893E-06	.77422E-04	.0004353	4.353	5.822	27.368
NA2O	62.0	.81978E-06	.50827E-04	.0002858	2.858	3.822	17.967
NA2CO3	106.0	.80610E-06	.85446E-04	.0004804	4.804	6.425	30.204
NAOH	40.0	.77306E-06	.30922E-04	.0001739	1.739	2.325	10.931
CUO	79.5	.76501E-06	.60818E-04	.0003420	3.420	4.573	21.499
CA	40.1	.76080E-06	.30508E-04	.0001715	1.715	2.294	10.784
ALN	41.0	.68672E-06	.28156E-04	.0001583	1.583	2.117	9.953
AL	27.0	.68672E-06	.18541E-04	.0001043	1.043	1.394	6.554
MG	24.3	.68664E-06	.16685E-04	.0000938	.938	1.255	5.898
VN	65.0	.68615E-06	.44600E-04	.0002508	2.508	3.354	15.766
V	51.0	.68606E-06	.34989E-04	.0001967	1.967	2.631	12.368
CAO	56.1	.66078E-06	.37070E-04	.0002084	2.084	2.788	13.104
BN	24.8	.63097E-06	.15648E-04	.0000880	.880	1.177	5.531
B	10.8	.63097E-06	.68145E-05	.0000383	.383	.512	2.409
V2O4	165.9	.60038E-06	.99603E-04	.0005600	5.600	7.490	35.209
NIO	74.7	.57533E-06	.42977E-04	.0002417	2.417	3.232	15.192
CR2O3	152.0	.56518E-06	.85907E-04	.0004830	4.830	6.460	30.367
CRCL2	122.9	.56503E-06	.69442E-04	.0003905	3.905	5.222	24.547
CR	52.0	.56493E-06	.29376E-04	.0001652	1.652	2.209	10.384
FE3O4	231.6	.56061E-06	.12984E-03	.0007300	7.300	9.764	45.896
K2O	94.2	.54027E-06	.50894E-04	.0002862	2.862	3.827	17.990
BE	9.0	.38195E-06	.34376E-05	.0000193	.193	.258	1.215
BEO	25.0	.37900E-06	.94751E-05	.0000533	.533	.713	3.349
PBO	223.2	.17941E-06	.40045E-04	.0002252	2.252	3.011	14.155
PB	207.2	.17934E-06	.37169E-04	.0002090	2.090	2.795	13.139
BE3N2	55.1	.12742E-06	.70207E-05	.0000395	.395	.528	2.482
SB	121.8	.53538E-07	.65209E-05	.0000367	.367	.490	2.305
SB2O3	291.5	.16081E-07	.46877E-05	.0000264	.264	.353	1.657

TABLE D-6. (Continued)

```
CAC2             64.1     .20000E-09    .12820E-07     .0000001        .001        .001        .005
CR3C2           183.1     .20000E-09    .36620E-07     .0000002        .002        .003        .013
SIC              40.1     .20000E-09    .80200E-09     .0000000        .000        .001        .003
TIC              59.9     .20000E-09    .11980E-07     .0000001        .001        .001        .004
K                39.1     .10000E-09    .39100E-08     .0000000        .000        .000        .001
NA               23.0     .10000E-09    .23000E-08     .0000000        .000        .000        .001
HG              200.6     .10000E-09    .20060E-07     .0000001        .001        .002        .007
MGCL2            95.2     .0            .0            0.0000000       0.000       0.000       0.000
                                                                                         ----------
                                                                                 TOTAL   1000000.00

                       (THE FOLLOWING GASEOUS SPECIES WERE PREDICTED)

SPECIES       MOL. WT.      MOLES          GRAMS      WT. PERCENT   PPM BY WT.   PPM BY WT.
                          (ASH+GAS)      (ASH+GAS)     (IN GAS)      (IN GAS)    (ASH+GAS)
----------   ----------   ----------     ----------    ----------    ---------   ----------
H2                2.0     .41947E+00     .83893E+00    6.7387362     67387.362    63086.715
CO               28.0     .32478E+00     .90939E+01   73.0470787    730470.787   683852.299
H2S              34.1     .70995E-02     .24209E+00    1.9445963     19445.963    18204.926
N2               28.0     .39620E-02     .11094E+00     .8910896      8910.896     8342.205
H2O              18.0     .32402E-02     .58323E-01     .4684821      4684.821     4385.836
CH4              16.0     .28026E-02     .44842E-01     .3601944      3601.944     3372.069
CO2              44.0     .11252E-02     .49508E-01     .3976707      3976.707     3722.914
K                39.1     .34878E-03     .13637E-01     .1095414      1095.414     1025.505
NA               23.0     .18192E-03     .41841E-02     .0336084       336.084      314.636
COS              60.1     .14899E-03     .89543E-02     .0719252       719.252      673.350
ZN               65.4     .34612E-04     .22636E-02     .0181823       181.823      170.219
P                31.0     .19515E-04     .60497E-03     .0048594        48.594       45.493
NH3              17.0     .49443E-05     .84053E-04     .0006752         6.752        6.321
CS2              76.1     .39685E-05     .30201E-03     .0024259        24.259       22.710
AS               74.9     .16003E-05     .11986E-03     .0009628         9.628        9.013
PBCL2           278.1     .72692E-06     .20216E-03     .0016238        16.238       15.202
TICL4           189.7     .39781E-06     .75464E-04     .0006062         6.062        5.675
BECL2            79.9     .38510E-06     .30769E-04     .0002472         2.472        2.314
PB              207.2     .34968E-06     .72454E-04     .0005820         5.820        5.448
SE               79.0     .22540E-06     .17807E-04     .0001430         1.430        1.339
CD              112.4     .18166E-06     .20419E-04     .0001640         1.640        1.535
ALCL3           133.3     .80729E-07     .10761E-04     .0000864          .864         .809
P4O10           283.9     .26786E-07     .76046E-05     .0000611          .611         .572
CDCL2           183.3     .10236E-07     .18762E-05     .0000151          .151         .141
HG              200.6     .87000E-08     .17452E-05     .0000140          .140         .131
S                32.1     .14025E-08     .45019E-07     .0000004          .004         .003
ZRCL4           233.1     .29224E-09     .68122E-07     .0000005          .005         .005
FE               55.9     .20265E-09     .11328E-07     .0000001          .001         .001
FE(OH)2          89.9     .44968E-10     .40426E-08     .0000000          .000         .000
BO               26.8     .22940E-10     .61478E-09     .0000000          .000         .000
CL2              70.9     .11418E-10     .80956E-09     .0000000          .000         .000
SO2              64.1     .68836E-11     .44124E-09     .0000000          .000         .000
BO2              42.8     .58990E-12     .25248E-10     .0000000          .000         .000
CDO             128.4     .13889E-12     .17834E-10     .0000000          .000         .000
KO               55.1     .26393E-13     .14543E-11     .0000000          .000         .000
ALOH             44.0     .45858E-14     .20177E-12     .0000000          .000         .000
SEO              95.0     .31282E-14     .29718E-12     .0000000          .000         .000
HGCL2           271.5     .26455E-15     .71826E-13     .0000000          .000         .000
HGO             216.6     .16267E-16     .35235E-14     .0000000          .000         .000
O2               32.0     .48433E-19     .15499E-17     .0000000          .000         .000
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TABLE D-6. (Continued)

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  SI                 28.1   .53939E-20   .15157E-18    .0000000        .000        .000
  SEO2              111.0   .13041E-22   .14475E-20    .0000000        .000        .000
  CA(OH)2            74.1   .18926E-23   .14024E-21    .0000000        .000        .000
  AS2O3             197.8   .25072E-24   .49592E-22    .0000000        .000        .000
                                         ----------  ----------  ----------  ----------
       TOTALS                            .12449E+02  100.000000  1000000.00  1000000.00
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TABLE D-7. TRACE ELEMENT DISTRIBUTION IN WELLMAN-GALUSHA GASIFIER AT 1200 F

(10 PERCENT BY WEIGHT OF THE FOLLOWING CONDENSED SPECIES ARE INCLUDED
IN THE PRODUCT GAS STREAM AS FLY ASH; THE BALANCE IS REMOVED AS ASH)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)	PPM BY WT. (IN ASH)
SIO2	60.1	.75779E-02	.45543E+00	.2334300	2334.300	22527.870	580623.533
FE	55.9	.29375E-02	.16421E+00	.0841645	841.645	8122.555	209347.207
CAS	72.2	.14727E-02	.10633E+00	.0544984	544.984	5259.534	135556.942
MGO	40.3	.17509E-03	.70563E-02	.0036167	36.167	349.039	8995.981
CACL2	111.0	.16750E-03	.18593E-01	.0095809	95.809	924.635	23831.134
TIO2	79.9	.12299E-03	.98267E-02	.0050367	50.367	486.081	12528.032
NA2CO3	106.0	.91519E-04	.97010E-02	.0049723	49.723	479.862	12367.767
AL2O3	101.9	.43143E-04	.43962E-02	.0022533	22.533	217.460	5604.719
B2O3	69.6	.39751E-04	.27667E-02	.0014181	14.181	136.855	3527.229
ZNO	81.4	.35051E-04	.28532E-02	.0014624	14.624	141.132	3637.463
MNO	70.9	.67268E-05	.47693E-03	.0002444	2.444	23.591	608.030
ZRO2	123.2	.50407E-05	.62102E-03	.0003183	3.183	30.719	791.732
NI	58.7	.24931E-05	.14634E-03	.0000750	.750	7.239	186.572
V2O4	165.9	.20584E-05	.34149E-03	.0001750	1.750	16.892	435.369
CU	63.5	.12759E-05	.80962E-04	.0000415	.415	4.005	103.217
TIN	61.9	.97610E-06	.60420E-04	.0000310	.310	2.989	77.029
TI	47.9	.97603E-06	.46755E-04	.0000240	.240	2.313	59.607
MN	54.9	.96095E-06	.52756E-04	.0000270	.270	2.610	67.258
C	12.0	.93452E-06	.11214E-04	.0000057	.057	.555	14.297
ALN	41.0	.92857E-06	.38072E-04	.0000195	.195	1.883	48.537
SI	28.1	.92515E-06	.25997E-04	.0000133	.133	1.286	33.143
ZRN	105.2	.90203E-06	.94894E-04	.0000486	.486	4.694	120.980
ZR	91.2	.84893E-06	.77422E-04	.0000397	.397	3.830	98.705
NA2O	62.0	.81712E-06	.50661E-04	.0000260	.260	2.506	64.588
CUO	79.5	.75501E-06	.60018E-04	.0000312	.312	3.008	77.537
BEO	25.0	.76409E-06	.19102E-04	.0000098	.098	.945	24.353
CAO	56.1	.75993E-06	.42632E-04	.0000219	.219	2.109	54.351
NA	23.0	.72633E-06	.16706E-04	.0000086	.086	.826	21.298
CR2O3	152.0	.70637E-06	.10737E-03	.0000550	.550	5.311	136.883
AL	27.0	.68672E-06	.18541E-04	.0000095	.095	.917	23.638
MG	24.3	.68664E-06	.16685E-04	.0000086	.086	.825	21.272
VN	65.0	.68616E-06	.44601E-04	.0000229	.229	2.206	56.861
V	51.0	.68606E-06	.34989E-04	.0000179	.179	1.731	44.607
K	39.1	.68332E-06	.26718E-04	.0000137	.137	1.322	34.062
K2O	94.2	.68014E-06	.64073E-04	.0000328	.328	3.169	81.686
CAC2	64.1	.64836E-06	.41560E-04	.0000213	.213	2.056	52.984
BN	24.8	.63097E-06	.15648E-04	.0000080	.080	.774	19.950
B	10.8	.63097E-06	.68145E-05	.0000035	.035	.337	8.688
NIO	74.7	.57533E-06	.42977E-04	.0000220	.220	2.126	54.791
FE3O4	231.6	.56061E-06	.12984E-03	.0000665	.665	6.422	165.528
ZN	65.4	.55636E-06	.36386E-04	.0000186	.186	1.800	46.388
NAOH	40.0	.53340E-06	.21336E-04	.0000109	.109	1.055	27.201
BE	9.0	.38195E-06	.34376E-05	.0000018	.018	.170	4.383
PB	207.2	.35883E-06	.74350E-04	.0000381	.381	3.678	94.788
CR	52.0	.28251E-06	.14690E-04	.0000075	.075	.727	18.729
PBCL2	278.1	.17949E-06	.49915E-04	.0000256	.256	2.469	63.637
CR3C2	183.1	.14146E-06	.25901E-04	.0000133	.133	1.281	33.021
CRCL2	122.9	.14128E-06	.17363E-04	.0000089	.089	.859	22.136

TABLE D-7. (Continued)

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BE3N2          55.1   .12742E-06   .70207E-05   .0000036     .036      .347       8.951
CD            112.4   .95950E-07   .10785E-04   .0000055     .055      .533      13.749
PBO           223.2   .89706E-07   .20022E-04   .0000103     .103      .990      25.526
SB            121.8   .53538E-07   .65209E-05   .0000033     .033      .323       8.313
CDCL2         183.3   .48025E-07   .88030E-05   .0000045     .045      .435      11.223
CDO           128.4   .47925E-07   .61536E-05   .0000032     .032      .304       7.845
SB2O3         291.5   .16081E-07   .46877E-05   .0000024     .024      .232       5.976
HG            200.6   .20725E-08   .41574E-06   .0000002     .002      .021        .530
VC             63.0   .20000E-09   .12600E-07   .0000000     .000      .001        .016
TIC            59.9   .20000E-09   .11980E-07   .0000000     .000      .001        .015
SIC            40.1   .20000E-09   .80200E-08   .0000000     .000      .000        .010
CA             40.1   .0           .0          0.0000000    0.000     0.000       0.000
MGCL2          95.2   .0           .0          0.0000000    0.000     0.000       0.000
                                                                             ----------
                                                                      TOTAL  1000000.00

                       (THE FOLLOWING GASEOUS SPECIES WERE PREDICTED)

SPECIES       MOL. WT.     MOLES        GRAMS      WT. PERCENT  PPM BY WT.  PPM BY WT.
                        (ASH+GAS)    (ASH+GAS)     (IN GAS)     (IN GAS)   (ASH+GAS)
----------   ----------  ----------   ----------   ----------   ----------  ----------
H2              2.0   .41171E+00   .82341E+00    4.2203959    42203.959   40730.218
CO             28.0   .29390E+00   .82293E+01   42.1792342   421792.342  407063.565
CO2            44.0   .15730E+00   .69213E+01   35.4749379   354749.379  342361.708
H2O            18.0   .12766E+00   .22979E+01   11.7780368   117780.368  113667.537
CH4            16.0   .48821E-01   .78114E+00    4.0037322    40037.322   38639.238
H2S            34.1   .70676E-02   .24101E+00    1.2352776    12352.776   11921.423
N2             28.0   .39578E-02   .11082E+00     .5679927     5679.927    5481.587
K              39.1   .34782E-03   .13600E-01     .0697048      697.048     672.707
COS            60.1   .19080E-03   .11467E-01     .0587735      587.735     567.212
NH3            17.0   .13102E-04   .22273E-03     .0011416       11.416      11.017
P4O10         283.9   .49056E-05   .13927E-02     .0071382       71.382      68.890
AS             74.9   .16003E-05   .11986E-03     .0006144        6.144       5.929
PB            207.2   .80739E-06   .16729E-03     .0008574        8.574       8.275
SE             79.0   .22540E-06   .17807E-04     .0000913         .913        .881
CS2            76.1   .77679E-07   .59114E-05     .0000303         .303        .292
NA             23.0   .82659E-08   .19012E-06     .0000010         .010        .009
HG            200.6   .67275E-08   .13495E-05     .0000069         .069        .067
FE(OH)2        89.9   .34493E-09   .31009E-07     .0000002         .002        .002
SO2            64.1   .87567E-11   .56131E-09     .0000000         .000        .000
BECL2          79.9   .64348E-11   .51414E-09     .0000000         .000        .000
S              32.1   .75460E-13   .24223E-11     .0000000         .000        .000
P              31.0   .48440E-13   .15017E-11     .0000000         .000        .000
TICL4         189.7   .26200E-14   .49702E-12     .0000000         .000        .000
ALCL3         133.3   .12545E-14   .16723E-12     .0000000         .000        .000
KO             55.1   .45113E-15   .24857E-13     .0000000         .000        .000
FE             55.9   .41033E-15   .22937E-13     .0000000         .000        .000
CL2            70.9   .18627E-15   .13206E-13     .0000000         .000        .000
SEO            95.0   .39755E-16   .37767E-14     .0000000         .000        .000
HGCL2         271.5   .23980E-17   .61397E-15     .0000000         .000        .000
BO2            42.8   .16804E-17   .71920E-16     .0000000         .000        .000
BO             26.8   .61050E-18   .16361E-16     .0000000         .000        .000
HGO           216.6   .23074E-18   .49979E-16     .0000000         .000        .000
ZRCL4         233.1   .27554E-19   .64229E-17     .0000000         .000        .000
AS2O3         197.8   .21243E-21   .42029E-19     .0000000         .000        .000
ALOH           44.0   .15730E-22   .69211E-21     .0000000         .000        .000
```

TABLE D-7. (Continued)

```
 O2              32.0    .52665E-23   .16853E-21    .0000000         .000         .000
 SEO2           111.0    .95231E-24   .61306E-22    .0000000         .000         .000
 CA(OH)2         74.1    .11799E-30   .87428E-29    .0000000         .000         .000
 SI              28.1    .11438E-35   .32141E-34    .0000000         .000         .000
                                      ----------  ----------   ----------   ----------
      TOTALS                          .19510E+02  100.000000   1000000.00   1000000.00
```

TABLE D-8. TRACE ELEMENT DISTRIBUTION IN RILEY-MORGAN GASIFIER AT 1250 F

(10 PERCENT BY WEIGHT OF THE FOLLOWING CONDENSED SPECIES ARE INCLUDED
IN THE PRODUCT GAS STREAM AS FLY ASH; THE BALANCE IS REMOVED AS ASH)

SPECIES	MOL. WT.	MOLES (ASH+GAS)	GRAMS (ASH+GAS)	WT. PERCENT (IN GAS)	PPM BY WT. (IN GAS)	PPM BY WT. (ASH+GAS)	PPM BY WT. (IN ASH)
SIO2	60.1	.75779E-02	.45543E+00	.3316912	3316.912	31547.277	580670.009
FE	55.9	.29375E-02	.16421E+00	.1195932	1195.932	11374.556	209363.988
CAS	72.2	.14728E-02	.10634E+00	.0774467	774.467	7365.987	135580.893
MGO	40.3	.17509E-03	.70563E-02	.0051391	51.391	488.783	8996.701
CACL2	111.0	.16826E-03	.18677E-01	.0136025	136.025	1293.741	23813.039
TIO2	79.9	.12299E-03	.98267E-02	.0071569	71.569	680.691	12529.035
NA2CO3	106.0	.91500E-04	.96990E-02	.0070639	70.639	671.846	12366.224
AL2O3	101.9	.43143E-04	.43962E-02	.0032018	32.018	304.524	5605.166
B2O3	69.6	.39751E-04	.27667E-02	.0020150	20.150	191.647	3527.511
ZNO	81.4	.35051E-04	.28532E-02	.0020780	20.780	197.636	3637.754
MNO	70.9	.67268E-05	.47693E-03	.0003473	3.473	33.036	608.078
ZRO2	123.2	.50407E-05	.62102E-03	.0004523	4.523	43.018	791.796
VC	63.0	.30879E-05	.19453E-03	.0001417	1.417	13.475	248.031
NI	58.7	.24931E-05	.14634E-03	.0001066	1.066	10.137	186.587
CU	63.5	.12750E-05	.80962E-04	.0000590	.590	5.608	103.226
TIN	61.9	.97610E-06	.60420E-04	.0000440	.440	4.185	77.036
TI	47.9	.97609E-06	.46755E-04	.0000341	.341	3.239	59.612
MN	54.9	.96095E-06	.52756E-04	.0000384	.384	3.654	67.264
ALN	41.0	.92859E-06	.38072E-04	.0000277	.277	2.637	48.542
SI	28.1	.92515E-06	.25997E-04	.0000189	.189	1.801	33.145
ZRN	105.2	.90203E-06	.94894E-04	.0000691	.691	6.573	120.989
ZR	91.2	.84893E-06	.77422E-04	.0000564	.564	5.363	98.713
NA2O	62.0	.81712E-06	.50661E-04	.0000369	.369	3.509	64.593
CUO	79.5	.76501E-06	.60818E-04	.0000443	.443	4.213	77.543
BEO	25.0	.76402E-06	.19100E-04	.0000139	.139	1.323	24.353
CAO	56.1	.75948E-06	.42607E-04	.0000310	.310	2.951	54.324
NA	23.0	.72633E-06	.16706E-04	.0000122	.122	1.157	21.299
CR2O3	152.0	.70637E-06	.10737E-03	.0000782	.782	7.437	136.894
AL	27.0	.68672E-06	.18541E-04	.0000135	.135	1.284	23.640
MG	24.3	.68664E-06	.16685E-04	.0000122	.122	1.156	21.274
VN	65.0	.68619E-06	.44601E-04	.0000325	.325	3.089	56.865
V	51.0	.68606E-06	.34989E-04	.0000255	.255	2.424	44.611
K	39.1	.65832E-06	.25718E-04	.0000195	.195	1.851	34.065
K2O	94.2	.67989E-06	.64046E-04	.0000466	.466	4.436	81.658
CAC2	64.1	.64783E-06	.41526E-04	.0000302	.302	2.876	52.945
BN	24.8	.63097E-06	.15648E-04	.0000114	.114	1.084	19.951
B	10.8	.63097E-06	.68145E-05	.0000050	.050	.472	8.688
C	12.0	.62658E-06	.75190E-05	.0000055	.055	.521	9.587
NIO	74.7	.57533E-06	.42977E-04	.0000313	.313	2.977	54.796
FE3O4	231.6	.56061E-06	.12984E-03	.0000946	.946	8.994	165.542
ZN	65.4	.55636E-06	.36386E-04	.0000265	.265	2.520	46.392
NAOH	40.0	.53340E-06	.21336E-04	.0000155	.155	1.478	27.203
V2O4	165.9	.51461E-06	.85374E-04	.0000622	.622	5.914	108.851
BE	9.0	.38195E-06	.34376E-05	.0000025	.025	.238	4.383
PB	207.2	.35883E-06	.74350E-04	.0000541	.541	5.150	94.796
CRCL2	122.9	.28253E-06	.34723E-04	.0000253	.253	2.405	44.271
PBCL2	278.1	.17949E-06	.49915E-04	.0000364	.364	3.458	63.642
CR3C2	183.1	.14146E-06	.25901E-04	.0000189	.189	1.794	33.024

TABLE D-8. (Continued)

```
     CR              52.0    .14125E-06    .73452E-05      .0000053       .053        .509       9.365
     BE3N2           55.1    .12742E-06    .70207E-05      .0000051       .051        .466       8.951
     CD             112.4    .95950E-07    .10785E-04      .0000079       .079        .747      13.751
     PBO            223.2    .89706E-07    .20022E-04      .0000146       .146       1.387      25.528
     SB             121.8    .53538E-07    .65209E-05      .0000047       .047        .452       8.314
     CDCL2          183.3    .48025E-07    .88030E-05      .0000064       .064        .610      11.224
     CDO            128.4    .47925E-07    .61536E-05      .0000045       .045        .426       7.846
     SB2O3          291.5    .16081E-07    .46877E-05      .0000034       .034        .325       5.977
     HG             200.6    .19170E-08    .38456E-06      .0000003       .003        .027        .490
     TIC             59.9    .20000E-09    .11980E-07      .0000000       .000        .001        .015
     SIC             40.1    .20000E-09    .80200E-08      .0000000       .000        .001        .010
     MGCL2           95.2    .0            .0             0.0000000      0.000       0.000       0.000
     CA              40.1    .0            .0             0.0000000      0.000       0.000       0.000
                                                                                              ----------
                                                                                   TOTAL  1000000.00

                               (THE FOLLOWING GASEOUS SPECIES WERE PREDICTED)

     SPECIES        MOL. WT.       MOLES         GRAMS      WT. PERCENT   PPM BY WT.    PPM BY WT.
                                 (ASH+GAS)     (ASH+GAS)     (IN GAS)      (IN GAS)     (ASH+GAS)
     ----------    ----------    ----------    ----------    ----------    ----------    ----------
     CO                  28.0    .30849E+00    .86378E+01    62.9093441    629093.441    598333.170
     H2                   2.0    .22422E+00    .44844E+00     3.2660208     32660.208     31063.248
     CH4                 16.0    .15994E+00    .25591E+01    18.6377915    186377.915    177264.746
     CO2                 44.0    .31386E-01    .13810E+01    10.0578818    100578.818     95660.897
     H2O                 18.0    .13429E-01    .24173E+00     1.7605332     17605.332     16744.498
     H2S                 34.1    .68621E-02    .23400E+00     1.7042127     17042.127     16208.832
     N2                  28.0    .39598E-02    .11087E+00      .8074950      8074.950      7680.115
     COS                 60.1    .39295E-03    .23616E-01      .1719995      1719.995      1635.894
     K                   39.1    .34782E-03    .13600E-01      .0990468       990.468       942.038
     NH3                 17.0    .90965E-05    .15464E-03      .0011263        11.263        10.712
     P4O10              283.9    .49056E-05    .13927E-02      .0101430       101.430        96.471
     CS2                 76.1    .17050E-05    .12975E-03      .0009450         9.450         8.987
     AS                  74.9    .16003E-05    .11986E-03      .0008730         8.730         8.303
     PB                 207.2    .80738E-06    .16729E-03      .0012184        12.184        11.588
     SE                  79.0    .22540E-06    .17807E-04      .0001297         1.297         1.233
     NA                  23.0    .45760E-07    .10525E-05      .0000077          .077          .073
     HG                 200.6    .68830E-08    .13807E-05      .0000101          .101          .096
     BECL2               79.9    .82816E-10    .66170E-08      .0000000          .000          .000
     FE(OH)2             89.9    .12066E-10    .10848E-08      .0000000          .000          .000
     P                   31.0    .56068E-11    .17381E-09      .0000000          .000          .000
     SO2                 64.1    .72621E-12    .46550E-10      .0000000          .000          .000
     TICL4              189.7    .35932E-12    .68163E-10      .0000000          .000          .000
     S                   32.1    .20645E-12    .66271E-11      .0000000          .000          .000
     ALCL3              133.3    .60371E-13    .80474E-11      .0000000          .000          .000
     FE                  55.9    .82624E-15    .46187E-13      .0000000          .000          .000
     CL2                 70.9    .60753E-15    .43074E-13      .0000000          .000          .000
     KO                  55.1    .18761E-15    .10337E-13      .0000000          .000          .000
     SEO                 95.0    .14318E-16    .13602E-14      .0000000          .000          .000
     HGCL2              271.5    .91172E-17    .24753E-14      .0000000          .000          .000
     ZRCL4              233.1    .52855E-17    .12320E-14      .0000000          .000          .000
     BO                  26.8    .34426E-17    .92261E-16      .0000000          .000          .000
     BO2                 42.8    .17170E-17    .73487E-16      .0000000          .000          .000
     HGO                216.6    .89201E-19    .19321E-16      .0000000          .000          .000
     ALOH                44.0    .10420E-21    .45849E-20      .0000000          .000          .000
     AS2O3              197.8    .38189E-23    .75539E-21      .0000000          .000          .000
```

TABLE D-8. (Continued)

```
O2                 32.0    .62866E-24    .20123E-22     .0000000          .000          .000
SEO2              111.0    .63058E-25    .69995E-23     .0000000          .000          .000
CA(OH)2            74.1    .11082E-31    .82117E-30     .0000000          .000          .000
SI                 28.1    .26421E-33    .74242E-32     .0000000          .000          .000
                                         ----------   ----------    ----------    ----------
     TOTALS                              .13731E+02   100.000000    1000000.00    1000000.00
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REFERENCES

(1) Cruise, D. R., J. Phys. Chem., 68, pp 3797-3802 (1964).

(2) Gordon, Sanford and McBride, Bonny J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions", "Rocket Performance, Incident, and Reflected Shocks", and "Chapman-Jouquet Detonations", NASA SP-273, 1971.

(3) Alexander, C. A., Hoyland, J. R., and Treweek, D. N., "Evaluation of Computerized Techniques for Predicting Chemical Reactivity and Stability", Final Report from Battelle's Columbus Laboratories to U.S. Coast Guard, DOT, April 11, 1975.

APPENDIX E

GAS CLEANUP SYSTEMS

APPENDIX E

GAS CLEANUP SYSTEMS

Scrubber Systems

A number of water scrubbing systems have been proposed for use with coal or oil gasification processes. These were shown in Appendix C. Such systems have been depicted as part of gasification systems in Figure C-4 for the Riley-Morgan gasifier system, in Figure C-5 for the Shell gasification process, and in Figure C-6 for the Texaco gasification process. Each of these scrubbing systems has different characteristics which are dependent upon the characteristics of the raw gas and the desired purity of the clean gas. Scrubber systems for other processes which have not been documented undoubtedly have differences in details of design but must be generically similar.

For the Riley-Morgan scrubber system (Figure C-4), a spray tower is followed in sequence by (1) a quench chamber, (2) a three-pass gas condenser, and (3) an electrostatic precipitator. The gas leaves the quench chamber at 76 C (169 F) and the gas condenser at 43 C (110 F). As will be discussed later, a temperature as high as 76 C (169 F) will not be conducive to the removal of ammonia. Also, there is no provision in the scrubbing liquor loop for the removal of the ammonia values. Thus, the ammonia concentration would be expected to build up to some steady-state concentration in the scrubbing liquor loop and, from that time on, there would be little change in ammonia concentration in the gas phase through the scrubber.

The scrubber shown associated with the Shell gasification process in Figure C-5 also has no provision for removal of contaminants such as ammonia in the scrubbing liquor loop. However, since this is a heavy oil gasifier, the ammonia content in the raw gas should be very low. A purge and a fresh water makeup stream do provide some capability for removal of contaminants.

The scrubber separator and water stripper shown as part of the Texaco gasification process in Figure C-6 is probably the most effective of the gas cleaning systems depicted from the standpoint of removal of impurities like ammonia and hydrogen cyanide. The water stripper should, as will be discussed later, drive off the gaseous impurities before the water is recycled to the scrubber. One deficiency appears to be that no cooling is performed on the stripped water which goes from the bottom of the stripper to the top of the scrubber. To provide effective srubbing (and cooling) there must be some provision in the water loop for cooling, although it is possible, for simplicity in the drawing, that this provision was omitted.

Raw Gas Compositions

Representative compositions of the raw gas leaving the heat recovery section of coal gasifiers are shown in Table E-1. The oxygen-blown case is based on a Koppers-Totzek gasifier. The concentrations of H_2, CO, CO_2, H_2S, and COS were based on the data for Illinois coal from Table C-1. The concentrations of H_2S and COS were adjusted to a coal sulfur content of 3.5 weight percent, based on the data in Table C-1. The concentrations of the five species listed above were then reduced proportionally to permit the addition of H_2O, NH_3, Ar, CH_4, and HCN, with these concentrations being directly obtained from Reference 19 of the text. The concentration of water vapor is fairly high (29 volume percent) because the Koppers-Totzek heat recovery system sprays water into the gas.

The particulate matter concentration in the Koppers-Totzek gas also is from Reference 19 and applies for coal containing about 10 percent ash. For this gasifier about half the ash in the coal goes into the gas. The operating temperature of the K-T gasifier is so high that very little tar is formed.

The air-blown case shown in Table E-1 is based on a Wellman-Galusha gasifier. The concentrations of H_2, CO, CO_2, CH_4, and N_2 were based on the data for bituminous coal from Table C-2. The concentrations of H_2S, COS, Ar, and HCN were estimated by adjusting the oxygen-blown data based on the fact that the gas production is 66 scf/lb coal for Wellman-Galusha air-blown and 31 scf/lb coal for Koppers-Totzek oxygen-blown. The NH_3 concentration was taken as 0.5 volume percent, reflecting the fact that

TABLE E-1. REPRESENTATIVE RAW GAS COMPOSITIONS

Specie	Concentration (mole % except as otherwise noted) Oxygen-Blown Gasifier (Koppers-Totzek)(a)	Air-Blown Gasifier (Wellman-Galusha)(b)
H_2	24.43	13.32
CO	39.08	25.39
CO_2	4.97	3.02
CH_4	0.08	2.40
H_2S	0.92	0.54
COS	0.08	0.02
NH_3	0.17	0.50
HCN	0.03	0.01
N_2	0.71	44.65
Ar	0.32	0.15
H_2O	29.19	10.00
	100.00	100.00
Tar (grains/scf)	---	3.82
Particulate matter (grains/scf)	11.57	0.1-0.5

(a) From data on Illinois coal (Table C-1) after adjustment to 3.5 percent S coal and addition of H_2O, NH_3, Ar, CH_4, and HCN from Reference 19 of the text.

(b) From data on bituminous coal (Table C-2) after addition of H_2O (assumed concentration), H_2S, COS, Ar, and HCN (adjusted from oxygen-blown data), and NH_3.

lower temperature gasifiers such as the Wellman-Galusha produce more NH_3 than the higher temperature Koppers-Totzek gasifier. Admittedly, the NH_3 concentration for the air-blown case (actually the lower temperature case) is not well defined.

For the Wellman-Galusha gas, the particulate matter and tar concentrations were based on data stating that the particulate matter in the gas comprise 1 to 5 percent of the ash in the coal and the tar in the gas about 3.6 weight percent of the moisture free coal.(1) The particulate matter concentration was calculated for a coal containing 10 percent ash.

Performance of Spray Towers

The performance of spray towers in the removal of ammonia from air have been explored by a number of investigators. Discussions of these investigations are contained in Perry(2) and in Sherwood and Pigford.(3) The most extensive investigation appears to be the one of Pigford and Pyle;(4) the information in this latter paper was used almost exclusively as the practical basis for the analysis performed to predict the removal of NH_3 and HCN from reducing gases produced from coal.

The performance of spray towers is dependent upon a number of variables. The characteristics of the spray, i.e., the droplet size and velocity, are very important. This means that the characteristics of the spray nozzle, the pressure drop through the nozzle, and the flow rate of the liquid will strongly affect the droplet characteristics and, therefore, the absorption characteristics of the column. Also of importance are the column diameter, the number of spray nozzles used, and their placement. If there is substantial interaction among the sprays from the various nozzles and if the sprays impact the walls so that a significant fraction of the liquid flows down the walls, then absorptive performance will be degraded. Thus, care must be taken in the design and operation of a spray absorption column that desired absorptive performance is achieved.

In the investigation reported by Pigford and Pyle,(4) ammonia absorption from air was measured in a 31.5-inch diameter spray tower. Tower heights were 52 inches and 26 inches in two distinct series of experiments. Gas inlet rates were varied from 218 to 817 lb/hr-sq ft and water inlet rates were varied from 285 to 955 lb/hr-sq ft. In the majority of experiments six Sprayco 5-B nozzles were used. Nozzle pressure drops varied from 2 to 35 lb/sq in. and were dependent upon the water inlet flow rates.

The number of overall gas-film transfer units, N_{OG}, was evaluated for each experiment run at constant conditions. It was found that N_{OG} (for a fixed tower height) increased approximately in proportion to the liquid rate and decreased as about the square root of the gas velocity. For the range of gas and liquid flow-rate conditions stated, experimental values for N_{OG} ranged from 0.30 to 2.43 for the 52-inch high column and from 0.29 to 1.31 for the 26-inch high column.

Further pertinent results and conclusions stated by Pigford and Pyle(4) relate to transfer unit height and maximum number of transfer units to be expected. They state that fewer transfer units per unit of height can be obtained in a tall chamber than in a short one. This is because longitudinal gas mixing is prevalent in spray towers and the gas may be so thoroughly mixed that it has nearly the same composition throughout. Thus, spray towers are limited to applications in which only 1 to 3 transfer units are required. If true countercurrent action were to be required from a spray-type unit, it would be necessary to collect the liquid at intervals of a few feet of tower height and respray it.

With this background, it becomes rather apparent that absorption by a spray tower would not be tremendously effective unless the liquid would be collected and resprayed several times; this technique, however, would appear to be precluded by the presence of the particulate matter which would almost certainly clog most known nozzle designs. With a single group of spray nozzles at the top of the scrubber, a common, practical and workable arrangement, the maximum number of transfer units achievable would appear to be about 3. This value has been selected as a basis for the subsequent analysis which is described.

Method of Computation

Mathematical Relations

Computational methods for determining the number of transfer units are succinctly described by Geankoplis.(5) He indicates [Equation (8.3-58)] that

$$N_{OG} = \left[\frac{(1-y)*M}{1-y}\right]_{ave} \int_{y_2}^{y_1} \frac{dy}{y-y*}$$

where y = mole fraction of gas being absorbed in the bulk gas

y* = mole fraction in the gas in equilibrium with the bulk liquid phase.

He also indicates that a simplification can be obtained if the solution is dilute and the equilibrium line is straight over the range of concentrations under consideration. Both of these conditions are true for the ammonia and hydrogen cyanide absorptions being evaluated here. Therefore, since

$$y* = mx$$

where m = slope of the equilibrium line at a constant temperature

x = mole fraction of absorbed gas in the bulk liquid

then

$$\int_{y_2}^{y_1} \frac{dy}{y-y*} = \frac{y_2-y_1}{\left[\dfrac{(y-y*)_1 - (y-y*)_2}{\ln \dfrac{(y-y*)_1}{(y-y*)_2}}\right]}$$

Furthermore,

$$\left[\frac{(1-y)*M}{1-y}\right]_{ave} = \frac{\dfrac{\left[\dfrac{(1-y_2^*) - (1-y_2)}{\ln \dfrac{(1-y_2^*)}{(1-y_2)}}\right]}{(1-y_2)} + \dfrac{\left[\dfrac{(1-y_1^*) - (1-y_1)}{\ln \dfrac{(1-y_1^*)}{(1-y_1)}}\right]}{(1-y_1)}}{2}$$

One further relationship is required before N_{OG} can be computed. This is the so-called "operating line". In reality, this is merely the equation which results from applying a material balance between the gas phase and the liquid phase in the absorption column. It can be stated as

$$X_2 = X_1 + \frac{(y_1-y_2)G}{(y_1-y_2)G + L}$$

G = gas flow rate, lb mole/hr-sq ft

L = liquid flow rate, lb mole/hr-sq ft.

Since, for the conditions of interest, the equations for computing N_{OG} can be expressed analytically, a direct computational procedure can be established. This was done and translated into a Fortran IV code for machine computation. A printout of this code is included at the end of this appendix.

Experimental Data

To permit computation, experimental values were needed for the slopes of the equilibrium lines for ammonia (NH_3) and hydrogen cyanide (HCN). These were obtained from literature sources. Data for NH_3 were obtained from Perry(2) and from Geankoplis.(5) Values used for computation were as follows:

Temperature, C	Slope of Equilibrium Line (for NH_3), m
30	1.198
40	1.936
50	2.791.

Data for HCN were obtained from Linke(6) and from International Critical Tables.(7) Values used were

Temperature, C	Slope of Equilibrium Line (for HCN), m
30 (30.2)	7.229
40 (40.2)	9.947
50	14.129.

As will be noted for the HCN values, actual temperatures for the reported data were 30.2 and 40.2 C. In all results, however, these are labelled 20 and 40 C, respectively.

Machine Computations

Computations utilizing the Fortran IV program previously mentioned were performed on Battelle's CDC 6400 computer. Specific values for G, L, y_1, y_2, and X_1, were selected and the number of transfer units (N_{OG}) computed. Nominal values for G and L were those representing maximum performance in the Pigford and Pyle(4) experiments. Variations in the L values were selected as twice and one-half the nominal value. All values used for computation are expressed with the results which are summarized in the following section.

Removal of NH_3 and HCN by Spray Towers

Computations were made for the range of conditions shown in Table E-2; the results obtained form the basis for the assessment of performance which is contained in this section.

A plot of results for removing ammonia from the raw gas is shown in Figure E-2. The number of transfer units, N_{OG}, for various inlet water ammonia concentrations is plotted versus the ammonia concentration in the outlet gas. Other factors are T = 30 C, G = 7.556 lb moles/hr-sq ft, L = 53.01 lb moles/hr-sq ft, and y_1 = 1700 ppmv. As will be observed, a greater number of transfer units is required to achieve a given exit gas concentration when the concentration of ammonia in the inlet water is higher. This is not unexpected behavior.

A series of these plots was constructed and then interpreted to obtain further performance estimates. For example, two additional plots

TABLE E-2. MAXIMUM EXPECTED REMOVALS OF NH_3 BY WATER SPRAY ABSORPTION TOWERS

(For Inlet Concentration of NH_3 in Water = 0)

Water Temperature, C	Liquid Rate, L, lb moles/hr-sq ft	Inlet Gas Concentration, ppmv	Outlet Gas Concentration, ppmv
30	26.505	1700	163
↓	53.01	↓	120
	106.02		101
30	26.505	5000	479
↓	53.01	↓	352
	106.02		296
40	26.505	1700	232
↓	53.01	↓	143
	106.02		112
40	26.505	5000	681
↓	53.01	↓	426
	106.02		330
50	26.505	1700	331
↓	53.01	↓	180
	106.02		126
50	26.505	5000	1071
↓	53.01	↓	529
	106.02		421

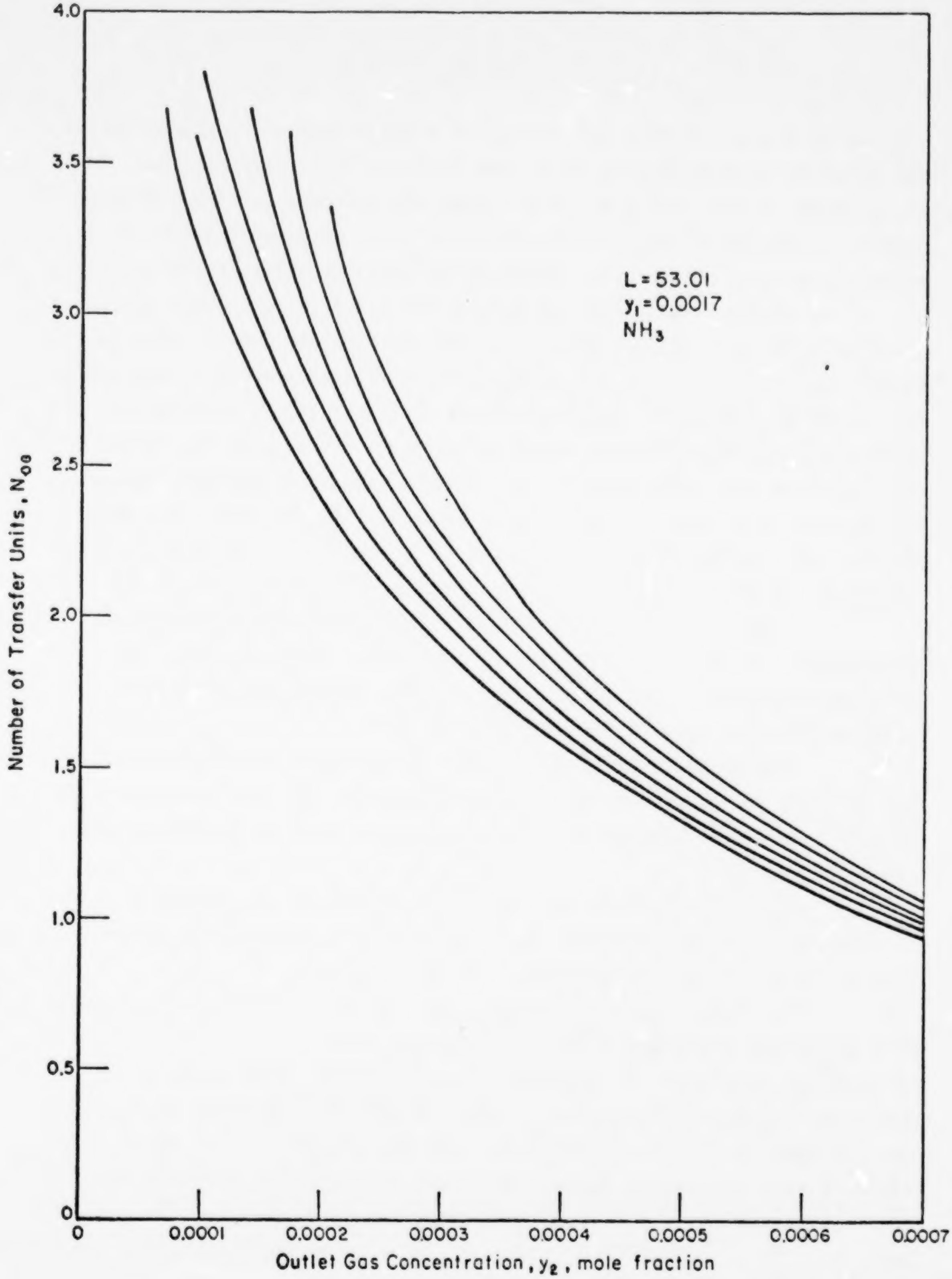

FIGURE E-2. NUMBER OF TRANSFER UNITS FOR AMMONIA REMOVAL similar to Figure E-2 were constructed at similar conditions except for the inlet water temperatures which were 40 C and 50 C, respectively. Then, recognizing, as previously discussed, that the probable maximum number of transfer units which could be achieved in a spray scrubber would be 3, cross plots were constructed. The first of these is shown in Figure E-3.

In Figure E-3, the ammonia concentration in the outlet gas is shown as a function of the ammonia concentration in the inlet scrubbing water. As stated, this is for an $N_{OG} = 3$ and an inlet ammonia concentration in the gas of 1700 ppmv. Smoothed curves (straight lines) through the points indicate the manner in which outlet gas concentration of ammonia will increase with inlet water concentration. Limiting (maximum) values for removal occur when the inlet water concentration of ammonia is zero. At 30 C, the minimum ammonia concentration in the outlet gas would be 115 ppmv. At 40 C it would be 140 ppmv and at 50 C, 180 ppmv.

Figure E-4 is a plot similar to Figure E-3 but for an inlet concentration of ammonia in the gas of 5000 ppmv. For this case, the minimum concentrations of ammonia in the outlet gas would be 350 ppmv at 30 C, 420 ppmv at 40 C, and 525 ppmv at 50 C.

Similar plots could be prepared for hydrogen cyanide removal. The behavior of the system would be similar except that the concentrations of HCN in the water streams entering and leaving would be much lower than those for NH_3.

In Table E-2, the maximum expected removals of ammonia for the variety of conditions which were computed are tabulated. A similar tabulation for hydrogen cyanide is shown in Table E-3.

In Tables E-2 and E-3, the liquid rates shown can be compared with those used experimentally by Pigford and Pyle.(4) The liquid rate of 53.01 lb moles/hr-sq ft corresponds to their L at their maximum L/G. The other two liquid rates used, 26.505 and 106.02 lb moles/hr-sq ft, were selected for these computational purposes as one-half and twice, respectively, the nominal value. The lower circulation rate would be less costly and the higher rate more costly for operation than the nominal one.

Inspection of the results Table E-2 indicates the penalty in removal efficiency resulting from higher operating temperatures. The

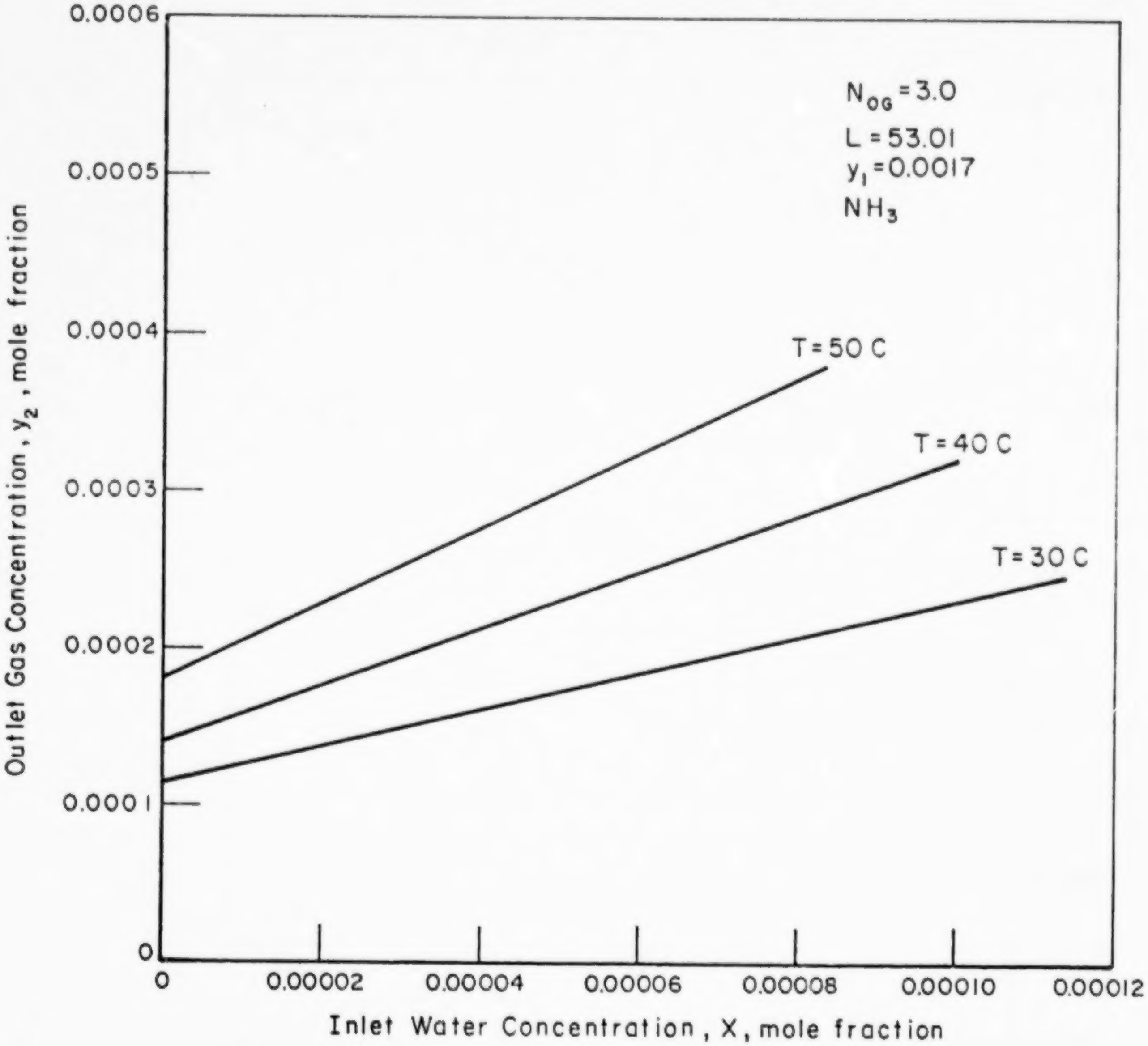

FIGURE E-3. OUTLET GAS AMMONIA CONCENTRATION AS A FUNCTION INLET WATER AMMONIA CONCENTRATION FOR AN INLET GAS AMMONIA CONCENTRATION OF 0.17 MOLE PERCENT (1700 ppmv)

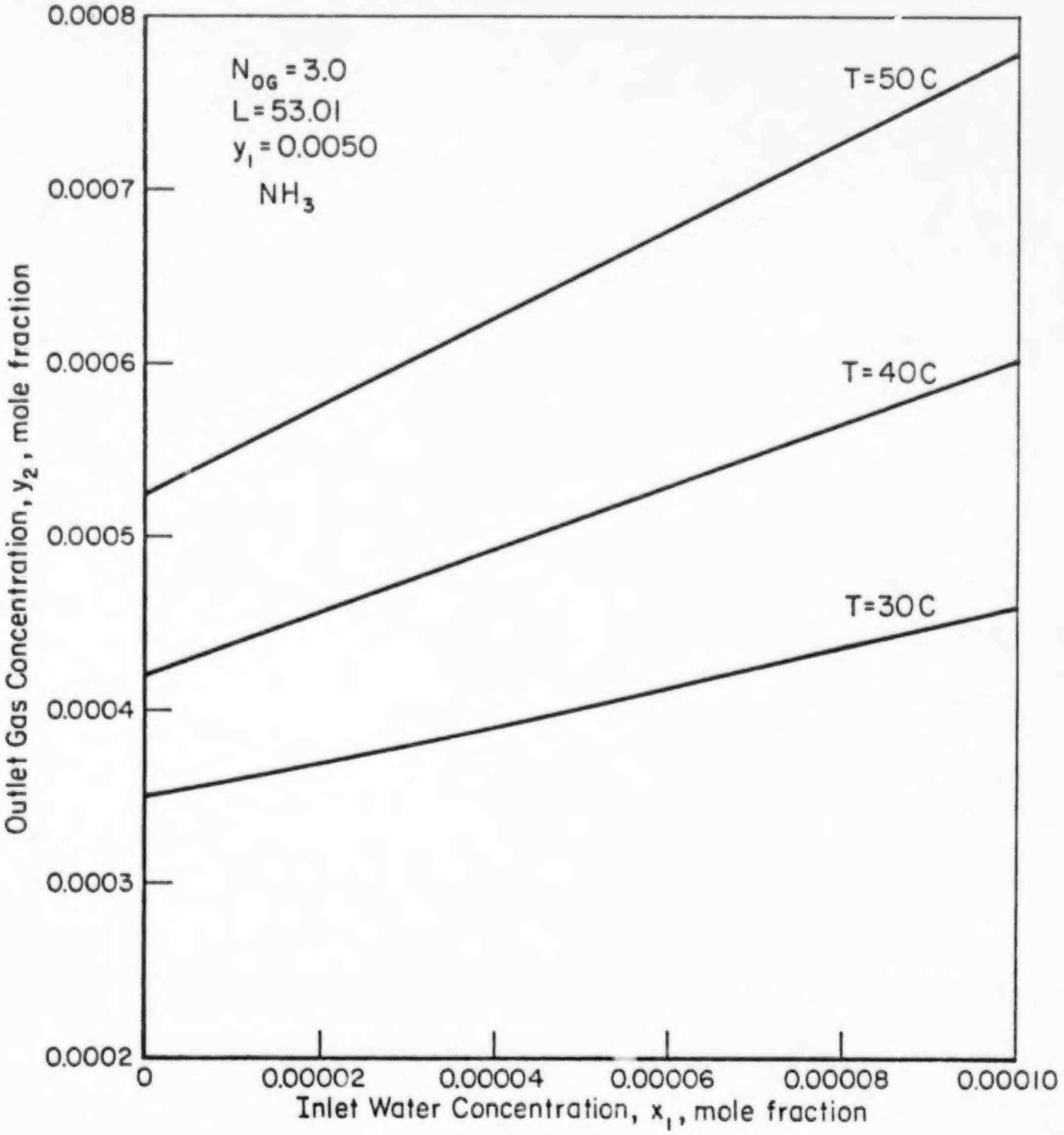

FIGURE E-4. OUTLET GAS AMMONIA CONCENTRATION AS A FUNCTION INLET WATER AMMONIA CONCENTRATION FOR AN INLET GAS AMMONIA CONCENTRATION FOR AN 0.50 MOLE PERCENT (5000 ppmv)

TABLE E-3. MAXIMUM EXPECTED REMOVALS OF HCN BY WATER SPRAY ABSORPTION TOWERS

(For Inlet Concentrations of HCN in Water = 0)

Water Temperature, C	Liquid Rate, L, lb moles/hr-sq ft	Inlet Gas Concentration, ppmv	Outlet Gas Concentration, ppmv
30	53.01	100	26
↓	106.02	↓	13
30	53.01	300	78
↓	106.02	↓	45
40	53.01	100	37
↓	106.02	↓	17
40	53.01	300	111
↓	106.02	↓	52
50	106.02	100	25
50	106.02	300	76

results also indicate that, with inlet ammonia concentrations of 1700 ppmv, outlet concentrations less than about 120 ppmv cannot be achieved in a single-stage scrubber. For an inlet concentration of 5000 ppmv the corresponding outlet concentration is about 352 ppmv.

In the computations for hydrogen cyanide removal, a number of the cases selected for computation did not result in operable conditions. This is indicated by the data contained in Table E-3, in which only the operable conditions are listed. The minimum outlet gas concentrations of HCN are about 26 ppmv with 100 ppmv at inlet and 78 ppmv with 300 ppmv at inlet.

Influence of H_2S on NH_3 Removal by Spray Towers

Subsequent to the performance of the above reported computations, a limited analysis was made to estimate the extent to which hydrogen sulfide (H_2S) would affect the absorption of ammonia (NH_3). This analysis also yielded information on the expected removal of H_2S from gas in a spray scrubber system.

The computer program previously described was modified to permit the simultaneous consideration of NH_3 and H_2S absorption. This involved a trial and error solution wherein a match of the number of transfer units for NH_3 and H_2S adsorption was sought by modifying the assumed extent of adsorption of H_2S.

Data for the computation were those derived by Beychok(8) from the work of Van Krevelen, et al.(9) The data used were those describing the simultaneous absorption of NH_3 and H_2S. No attempt was made to consider the influence of the presence of CO_2 in this system even though data are available from the work of Van Krevelen, et al.(9) Consideration of CO_2 absorption along with that for NH_3 and H_2S could easily have introduced an order of magnitude of complexity into the computational procedure. This did not appear warranted.

Results of the computations are shown in Tables E-4 and E-5. In both tables the absorption of NH_3 when influenced by simultaneous absorption of H_2S is compared with the absorption of NH_3 when it was assumed that there was no influence of H_2S. These latter results are those

TABLE E-4. ABSORPTION COMPARISONS AT 1.5 TRANSFER UNITS FOR $y_1(NH_3)$ = 0.0017 and $y_1(H_2S)$ = 0.0092

$x_1(NH_3)$	$y_2(NH_3)$(a)	Previous $y_2(NH_3)$(b)	$x_1(H_2S)$	$y_2(H_2S)$(a)
		L = 53.01, T = 30 C		
0.00002	0.000393	0.000445	0.000004	0.001642
0.00004	0.000409	0.000463	0.000008	0.001645
0.00006	0.000413	0.000481	0.000012	0.001583
0.00008	0.000420(c)	0.000499	0.000016	0.001573(c)
0.00010	0.000436	0.000517	0.000020	0.001569
		L = 106.02, T = 30 C		
0.00002	0.000391	0.000421	0.000004	0.001838
0.00004	0.000402	0.000439	0.000008	0.001789
0.00006	0.000414	0.000458	0.000012	0.001787
0.00008	0.000425	0.000476	0.000016	0.001801
0.00010	0.000463	0.000495	0.000020	0.001924
		L = 53.01, T = 40 C		
0.00002	0.000411	0.000486	0.000004	0.001384
0.00004	0.000417	0.000515	0.000008	0.001291
0.00006	0.000438	0.000543	0.000012	0.001293
0.00008	0.000442(c)	0.000571	0.000016	0.001188(c)
0.00010	0.000449(c)	0.000600	0.000020	0.001131(c)
		L = 106.02, T = 40 C		
0.00002	0.000400	0.000447	0.000004	0.001647
0.00004	0.000416	0.000477	0.000008	0.001619
0.00006	0.000433	0.000505	0.000012	0.001603
0.00008	0.000452	0.000535	0.000016	0.001590

(a) Values obtained considering the simultaneous absorption of NH_3 and H_2S.

(b) Values computed ignoring influence of H_2S absorption.

(c) Underline indicates linearly extrapolated values; all other values were linearly interpolated.

TABLE E-5. ABSORPTION COMPARISON AT 1.5 TRANSFER UNITS FOR $y_1(NH_3)$ = 0.0050 and $y_1(H_2S)$ = 0.0054

$x_1(NH_3)$	$y_2(NH_3)$(a)	Previous $y_2(NH_3)$(b)	$x_1(H_2S)$	$y_2(H_2S)$(a)
		L = 106.02, T = 30 C		
0.00006	0.001160	0.001308	0.000012	0.001758
0.00008	0.001117(c)	0.001327	0.000016	0.001656(c)
0.00010	0.001175	0.001345	0.000020	0.001632

(a) Values obtained considering the simultaneous absorption of NH_3 and H_2S.

(b) Values computed ignoring influence of H_2S absorption.

(c) Underline indicates linearly extrapolated values; all other values were linearly interpolated.

previously discussed. Table E-4 covers inlet gas concentrations of 1700 ppmv for NH_3 and 9200 ppmv for H_2S; Table E-5 is for concentrations of 5000 ppmv for NH_3 and 5400 ppmv for H_2S. Comparisons were made at 1.5 transfer units because valid solutions could not be obtained at higher values (i.e., 3.0 as used previously).

Inspection of the results indicates that the additional absorption of NH_3 obtained when considering the simultaneous absorption of H_2S is not significant. Only about 3 percent more NH_3 is absorbed. However, there are significant amounts of H_2S removed. However, the amounts of H_2S absorbed would probably be reduced to some extent in any actual situation by the simultaneous absorption of CO_2.

It is concluded that the results obtained for NH_3 absorption in the calculations where the simultaneous absorption of H_2S was ignored are reasonably valid.

There may also be an interaction between NH_3 and HCN, since these compounds are known to form NH_4CN in the liquid phase. However, the concentrations of HCN are so low that an investigation of this interaction did not appear warranted.

Stripping Column Performance

A major question in attempting to predict the extent of removal of ammonia and hydrogen cyanide in a spray scrubber is that pertaining to the concentrations in the inlet scrubbing water of the species being removed. In an attempt to answer this question, some exploratory computations were performed to evaluate the ease with which ammonia can be stripped from water. Computational techniques presented by Robinson and Gilliland(10) and data from Perry(2) were utilized. Because of the exploratory nature of the computations, the techniques and data will not be described here.

Results of the computations indicate that ammonia can be easily stripped from water. Less than two equivalent plates would be needed in the stripping section of the column to achieve an ammonia concentration in the recycle water stream of 1 ppm (mole fraction of 0.000001). This is substantially zero and should permit achieving within about 5 ppm of the minimum gas phase ammonia concentrations shown in Table E-3. With more equivalent plates in the stripping section, even lower ammonia concentrations could be obtained, which would result in an even closer approach to the minimum values shown in Table E-3.

Similar computations were not made for hydrogen cyanide; this could be accomplished, however, if there were sufficient interest.

Conclusions

Computations performed have indicated that substantial amounts of ammonia and hydrogen cyanide are removed by spray scrubbers which are installed primarily to achieve tar, tar oil, naphtha, and particulate removal. Despite substantial removal of NH_3 and HCN by water scrubbers, however, there are still significant amounts remaining in the cleaned gas. These amounts are shown in Table E-2 for ammonia and Table E-3 for hydrogen cyanide.

There are several ways, not explored computationally, in which modifications to the scrubber design, operation, or conditions might result in greater removals of ammonia and hydrogen cyanide. Three of these ways worthy of mention are:

- Increasing water circulation rates
- Increasing the number of transfer units by collecting and respraying water
- Using lower water temperatures.

Each of these ways would result in a more costly operation but substantial benefit might be achieved.

Of the three improvement methods listed, increasing the number of transfer units by collecting and respraying the water would probably be the most effective. Some difficulty would probably be encountered, however, with particulate matter clogging the spray nozzles. Such problems could probably be overcome by including filters in the respray loop and by using nonclogging spray heads.

Additional computations to determine more extensively the behavior of scrubbing systems could be performed and would probably be worthwhile.

Computer Program for Number of Transfer Units

This section contains the FORTRAN computer program used for calculating the number of transfer units (N_{OG}) for gas washing equipment.

```
      PROGRAM LEMMON(OUTPUT)
C
C
C     PROGRAM LEMMON
C
C
C     PURPOSE - CALCULATE TRANSFER UNITS FOR AMMONIA AND
C               HYDROGEN CYANIDE  IN A SPRAY COLUMN
C
C
C     WRITTEN FOR - A.H. LEMMON, BATTELLE MEMORIAL INSTITUTE
C
C
C     AUTHOR - ROSS R. PAVLAC
C                   SYSTEMS PROGRAMMER, BATTELLE MEMORIAL INSTITUTE
C
C
C     WRITTEN - NOVEMBER 17, 1975
C
C
C     VARIABLES USED -
C
C
C     G       - GAS    RATE IN LB.-MOLES/HR-SQ.FT
C
C     L       - LIQUID RATE IN LB.-MOLES/HR-SQ.FT
C
C     M       - SLOPE OF EQUILIBRIUM LINE
C
C     NOG     - NUMBER OF TRANSFER UNITS
C
C     X1      - LIQUID INLET CONCENTRATION
C
C     X2      - LIQUID OUTLET CONCENTRATION
C
C     Y1      - INLET GAS CONCENTRATION
C
C     Y2      - OUTLET GAS CONCENTRATION
C
C
C
      REAL L,M,Y1ARR(4),INY2Y1,NOG
      REAL LARR(3),MARR(6),MC(3,6)
      DATA LARR/53.01,105.02,26.505/
      DATA MARR/1.198413,1.935810,2.790584,7.229038,9.947156,14.12948258
     1/
      DATA MC/    4HNH3 ,4HAT 3,2H0C,4HNH3 ,4HAT 4,2H0C,
     1  4HNH3 ,4HAT 5,2H0C,4HHCN ,4HAT 3,2H0C,
     2  4HHCN ,4HAT 4,2H0C,4HHCN ,4HAT 5,2H0C   /
      DATA Y1ARR/0.0017,0.0050,0.0003,0.0001/
      DATA G/7.536/
C
C
C         MAIN LOOP - VARY SLOPE OF EQUILIBRIUM LINE
C
C
```

```
      DO 1000 KINDEX =1,6
      M = MARP(KINDEX)
      LNCNT=55
C
C         VARY LIQUID RATE
C
      DO 1000 IINDEX=1,3
      L=LARR(IINDEX)
C
C
C         VARY LIQUID INLET CONCENTRATION
C
C
C         IF NH3, VARY BY INCREMENTS OF .00002
C         IF HCN, VARY BY INCREMENTS OF .000002
C
      X1=-0.00002
      X1INC = 0.00002
      IF(KINDEX .LE. 3) GOTO 110
      X1 = -0.000002
      X1INC = 0.000002
  110 CONTINUE
      DO 1000 JINDEX = 1,6
      X1=X1+X1INC
C
C     VARY INLET GAS CONCENTRATIONS
C
      LMIN=1
C         IF HCN (KINDEX =4 THRU 6), USE A DIFFERENT SET OF INLET GAS
C              CONCENTRATIONS
      IF(KINDEX.GT.3) LMIN=3
      LMAX=LMIN+1
      DO 1000 LINDEX=LMIN,LMAX
      Y1=Y1ARR(LINDEX)
C
C
C         VARY OUTLET GAS CONCENTRATIONS
C
C
      YINC=0.0
      DO 1000 MINDEX=1,25
      YINC=YINC+0.02
      Y2 = YINC * Y1
C
C     CHECK IF Y2 IS OUT OF RANGE
C
      IF(Y2 .GE. M * X1) GOTO 200
C           DEBUGGING CODE CAN GO HERE
      GOTO 1000
  200 CONTINUE
C
C
C
      X2 = (( (Y1-Y2) * G) / ( ((Y1-Y2) * G) + L) ) + X1
      YE1 = M * X2
C
```

```
C          CHECK THE VALIDITY OF Y1
C
      IF(Y1 .GE. YE1 ) GOTO 300
C          DEBUGGING CODE CAN GO HERE
      GOTO 1000
  300 CONTINUE
C
C     WE ARE AT THE LOW POINT OF THE LOOP.
C     ACTUAL COMPUTATION BEGINS HERE
C
C
      YE2 = M * Y1
      QUANT1 = ALOG( (1.-YE2)/(1.-Y2) )
      QUANT2 = ALOG( (1.-YE1)/(1.-Y1) )
      Y1MYE1= Y1 - YE1
      Y2MYE2 = Y2 - YE2
      AVQUOT = ( ( Y2MYE2 / QUANT1 ) +
     1    ( Y1MYE1 / QUANT2 ) ) / 2.
      INY2Y1 = (Y1-Y2) / ( (Y1MYE1 - Y2MYE2) /
     1 ( ALOG( Y1MYE1 / Y2MYE2 ) ) )
      NOG = AVQUOT * INY2Y1
C
C
C          PRINT OUT THE ANSWERS
C
C
      LNCNT=LNCNT +1
      IF(LNCNT.LE.51) GOTO 850
      LNCNT=1
      PRINT 820
  820 FORMAT(1H1,4X,8HGAS RATE,3X,
     1               11HLIQUID RATE,4X,12HLIQUID INLET,
     1 1X,13HLIQUID OUTLET,5X,8HSLOPE OF, 5X, 13HCOMPOUND/TEMP,
     2 3X,9HINLET GAS,5X, 10HOUTLET GAS, 2X, 8HTRANSFER /
     2 1H , 16HLB-MOLES/HR-SQFT,1X,
     3      16HLB-MOLES/HR-SQFT, 1X, 13HCONCENTRATION, 1X,
     4 13HCONCENTRATION, 1X, 16HEQUILIBRIUM LINE, 15X, 13HCONCENTRATION
     5, 1X, 13HCONCENTRATION, 1X, 7H  UNITS / 1H 16(1H-),1X,
     6     16(1H-),1X,13(1H-),1X,13(1H-),1X,16(1H-),
     7 1X,13(1H-),1X, 13(1H-),1X, 13(1H-),1X, 8(1H-),/)
  850 CONTINUE
      PRINT 900,G,L,X1,X2,M,(MC(II,KINDEX),II=1,3),Y1,Y2,NOG
  900 FORMAT(1X,2X,F10.5,8X,F10.5, 5X,F12.7,1X, F12.7,3X,F10.5 ,7X,
     1 A4,A4,A2,2X,F10.5,4X,F12.7,      F11.5      )
 1000 CONTINUE
C
C          COMPUTATION IS FINISHED
C
      STOP
      END
```

E-25 and E-26

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APPENDIX F

DETAILS ON ENGINEERING ANALYSIS

APPENDIX F

DETAILS ON ENGINEERING ANALYSIS

This appendix contains additional details related to the engineering analyses made as part of this project.

Quantity of Reductant Required

Basis: 1000-MW power plant
Coal heating value = 12,000 Btu/lb
Coal sulfur content = 3.5 weight percent
Power plant heat rate = 9,750 Btu/kWh (35% efficiency).

Hourly coal burning rate to generate electricity

$$= 10^6 \text{ kW} \times 9{,}750 \text{ Btu/kWh} \times \text{lb coal}/12{,}000 \text{ Btu} \times \text{ton}/2000 \text{ lb} = 406.25 \text{ ton/hr.}$$

Sulfur burned per hour

$$= 406.25 \times 0.035 = 14.22 \text{ ton/hr.}$$

SO_2 generated per hour

$$= \frac{64.06\ SO_2}{32.06\ S} \times 14.22 = 28.41 \text{ ton/hr or } 887.0 \text{ lb-mole/hr.}$$

Reduction of one mole of SO_2 to sulfur requires 2 moles of reductant (H_2 + CO + H_2S). The FGD process will remove about 90 percent of the SO_2 from the flue gas. Some reductant in excess of the stoichiometric amount will be required to insure a high SO_2 conversion. Using about 11 percent excess reductant, the moles of reductant required can be taken as twice the moles of SO_2 generated by the power plant. That is,

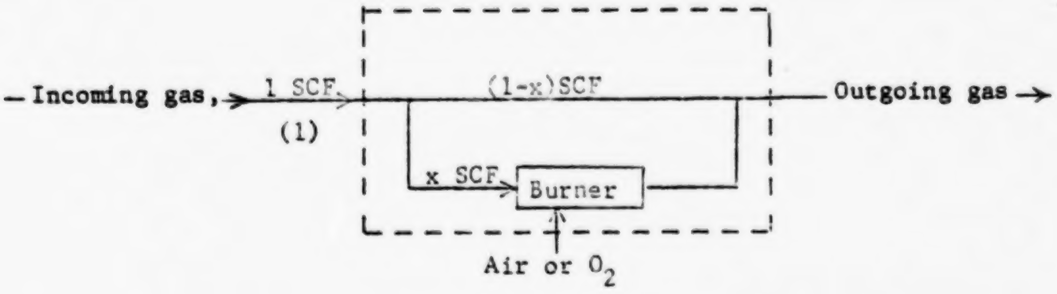
$$\text{Reductant } (H_2 + CO + H_2S) \text{ requirement} = 2 \times 887.0 = 1{,}774.0 \text{ lb-mole/hr.}$$

$$\text{or } 1{,}774 \times 359.2 \text{ scf/lb-mole} \times \text{hr}/60 \text{ min} = 10{,}620 \text{ scfm.}$$

This does not include the gas which must be burned to reheat the reducing gas. This is discussed in the following section.

Quantity of Reducing Gas Burned to Reheat Gas

When the water wash step is followed by a high temperature step, as it is for the application to Type A FGD processes, the reducing gas must be reheated. To reach a temperature around 340 C (650 F), the most efficient method will normally be to burn a portion of the gas. The amount of gas which must be burned and the effects on the final reducing gas composition are determined by material and energy balances around the burner system, as follows:



x = fraction of incoming gas which is burned.

The basis for the calculations presented here is as follows:

(1) The incoming gas is at 30 C (86 F) and the outgoing gas at 343 C (650 F).

(2) For the gas produced by an oxygen-blown gasifier, the burner is also fired with oxygen. For the air-blown gasifier the burner is fired with air.

(3) 10 percent excess oxygen or air is supplied to the burner.

Tables F-1 and F-2 show the material and energy balances for the oxygen-blown and air-blown cases, respectively. The quantity of gas which must be burned is 4.50 percent of the incoming gas for the oxygen-blown case and 8.65 percent for the air-blown case.

Flue Gas Quantity and Reheat Requirement

The applicable combustion reactions are

$$C + O_2 \rightarrow CO_2$$

$$H_2 + 1/2\ O_2 \rightarrow H_2O$$

$$S + O_2 \rightarrow SO_2$$

$$N + 1/2\ O_2 \rightarrow NO.$$

On the basis of 100 pounds of coal, the quantities involved are

C	70.5 lb	or	5.88 lb atoms
H	5.0 lb		2.50 lb-moles
S	3.5 lb		0.11 lb atoms
N	1.5 lb		0.05 lb-moles
O	8.8 lb		0.28 lb-moles.

The theoretical amount of reaction products after combustion is

$$5.88 + 2.50 + 0.11 + 0.05 = 8.54 \text{ lb-moles/100 lb coal.}$$

The theoretical amount of oxygen required (neglecting that in the coal) is

$$5.88 + (1/2)(2.50) + 0.11 + (1/2)(0.05) = 7.27 \text{ lb-moles/100 lb coal.}$$

At 20 percent excess air, the total air required is

$$7.27 \times 1/0.21 \times 1.2 = 41.51 \text{ lb-moles/100 lb coal.}$$

On combustion, the 7.27 lb-moles of oxygen which reacts yields 8.54 lb-moles of reaction products. Thus, the total moles of reaction products (including inerts in the air) is

$$41.51 + (8.54 - 7.27) = 42.78 \text{ lb-moles/100 lb coal}$$

or 855.6 lb-moles/ton of coal.

TABLE F-1. MATERIAL AND ENERGY BALANCES AROUND REHEAT SYSTEM FOR OXYGEN-BLOWN GASIFIER

Basis: 1 scf Incoming Gas, x = Fraction of Incoming Gas Burned

	Incoming Gas at 30 C (86 F)			Oxygen for Combustion at 21 C (70 F)			Outgoing Gas at 343 C (650 F)		
Specie	scf	Btu/scf	Btu	scf	Btu/scf	Btu	scf	Btu/scf	Btu
H_2	0.3065	0.474	0.1453				0.3065 (1-x)	10.830	3.3194 (1-x)
CO	0.4903	0.484	0.2373				0.4903 (1-x)	11.045	5.4154 (1-x)
CO_2	0.0624	0.605	0.0378				0.0624 + 0.4913x	15.945	0.9950 + 7.8338x
CH_4	0.0010	0.615	0.0006				0.0010 (1-x)	17.520	0.0175 (1-x)
H_2O	0.1152	0.552	0.0636				0.1152 + 0.3085x	12.960	1.4930 + 3.9982x
Other	0.0246	0.478	0.0118	0.0090x	0.282	0.0025x	0.0246 + 0.0090x	10.975	0.2700 + 0.0988x
O_2	———		———	0.4415x	0.282	0.1245x	0.0401x	11.415	0.4577x
Total	1.000		0.4964	0.4505x		0.1270x	1.0000 + 0.0511x		11.5103 + 3.6362x

Energy Balance: (Incoming Gas) + (Oxygen for Combustion) + (Heat of Combustion) = (Outgoing Gas)

$$0.4964 + 0.1270x + 248.14x = 11.5103 + 3.6362x$$

$$x = \frac{11.0139}{244.63} = 0.0450.$$

Amount of 98 percent oxygen required = (0.4505)(0.0450) = 0.0203 scf.

Amount of outgoing gas = 1 + (0.0511)(0.0450) = 1.0023 scf.

TABLE F-2. MATERIAL AND ENERGY BALANCES AROUND REHEAT SYSTEM FOR AIR-BLOWN GASIFIER

Basis: 1 scf Incoming Gas, x = Fraction of Incoming Gas Burned

Specie	Incoming Gas at 30 C (86 F)			Air for Combustion at 21 C (70 F)			Outgoing Gas at 343 C (650 F)		
	scf	Btu/scf	Btu	scf	Btu/scf	Btu	scf	Btu/scf	Btu
H_2	0.1318	0.474	0.0625				0.1318 (1-x)	10.830	1.4274 (1-x)
CO	0.2511	0.484	0.1215				0.2511 (1-x)	11.045	2.7734 (1-x)
CO_2	0.0299	0.605	0.0181				0.0299 + 0.2748x	15.945	0.4768 + 4.3817x
CH_4	0.0237	0.615	0.0146				0.0237 (1-x)	17.520	0.4152 (1-x)
H_2O	0.1152	0.552	0.0636				0.1152 + 0.1792x	12.960	1.4930 + 2.3224x
Other	0.4483	0.478	0.2143				0.4483 + 0.9615x	10.975	4.9201 + 10.5525x
Air				1.3753x	0.291	0.4002x	0.1250x	11.035	1.3796x
Total	1.000		0.4946	1.3753x		0.4002x	1.0000 + 1.1339x		11.5059 + 14.0202x

Energy Balance: (Incoming Gas) + (Air for Combustion) + (Heat of Combustion) = (Outgoing Gas)

$$0.4946 + 0.4002x + 140.94x = 11.5059 + 14.0202x$$

$$x = \frac{11.0113}{127.32} = 0.0865.$$

Amount of air required = (1.3753)(0.0865) = 0.1190 scf.

Amount of outgoing gas = 1 + (1.1339)(0.0865) = 1.0981 scf.

F-7 and F-8

Quantity of Heat for Reheating Flue Gas After Scrubbing

The quantity of heat required to reheat the flue gas after scrubbing can be estimated as follows. The flue gas usually must be reheated to about 93 C (200 F) in order to provide adequate plume buoyancy and to avoid condensation in the stack. Using a psychrometric chart for air, the difference in enthalpy between 93 C (200 F) and 52 C (125 F) at constant absolute humidity is about 21 Btu/lb. Since the molecular weight of the flue gas is about 29, the heat required to reheat the flue gas from 52 C (125 F) to 93 C (200 F) is

$$\frac{855.6 \text{ lb-moles}}{\text{ton coal}} \; \frac{29 \text{ lb}}{\text{lb-moles}} \; \frac{21 \text{ Btu}}{\text{lb}} = 521{,}000 \text{ Btu/ton coal.}$$

If the coal has a heating value of 12,000 Btu/lb, the flue gas reheat requirement represents about 2.2 percent of the energy in the coal input.

APPENDIX G

SOURCES OF COST INFORMATION

APPENDIX G

SOURCES OF COST INFORMATION

Coal Gasification Systems

This section includes cost information on a number of coal gasification systems. A consensus of these data was used in developing the costs used in this report. The consensus will be discussed after each source of cost data is discussed individually. The investment data are compared in Figure G-1, where they are plotted against the production rate of reducing gases, i.e., H_2, CO, and H_2S (CH_4 is not considered sufficiently reactive).

Wellman-Galusha, Air Blown

The basic cost data for Wellman-Galusha gasification systems were taken from the brochure "Introduction of a Modernized Concept for Utilization of a Low-Btu Coal Gasification Unit", which was prepared by Mason & Hangar and McDowell-Wellman in June, 1974. This brochure gave the investment for a gasification system including one gasifier, a cyclone for particulate matter removal, coal preparation facilities, and a small control building. These data are shown in Table G-1. Also shown in this table is the extension of these data to a system involving five gasifiers, this being based on information obtained from McDowell-Wellman Engineering Company in May, 1975.(1) This information was that the additional gasifiers would cost $400,000 apiece and that the five-fold capacity increase would increase the coal preparation facilities cost by $240,000. These costs do not include water washing of the gas, since the data did not permit separating this from the H_2S removal cost.

Wellman-Galusha, Oxygen Blown

A quotation was obtained from Mason & Hangar in 1975 on a gasification system involving three 10-foot diameter oxygen-blown Wellman-

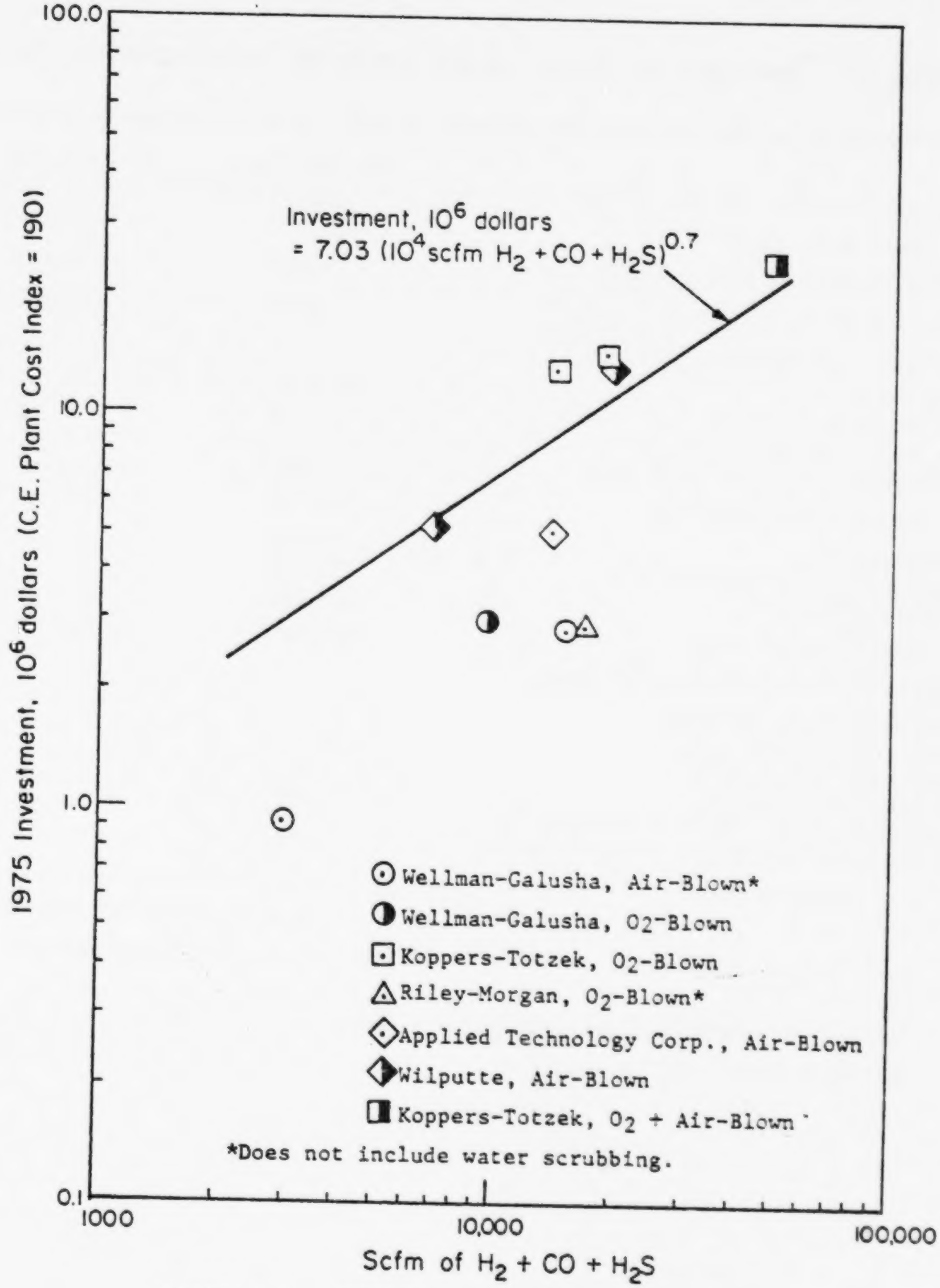


FIGURE G-1. INVESTMENT FOR GASIFICATION SYSTEMS
Includes Water Scrubbing But Not
H_2S Removal or Oxygen Plant

TABLE G-1. COST DATA FOR WELLMAN-GALUSHA AIR-BLOWN GASIFICATION SYSTEMS

	One Gasifier	Five Gasifiers
Coal Input Rate, lb/hr	7,000	35,000
Dry Gas Production Rate, scfm(a)	7,580	37,900
Production of $H_2 + CO + H_2S$, scfm(b)	2,980	14,900
Investment, escalated to 1/1/75,(c) $		
Equipment	541,559	
Erection (equipment)	25,860	
Control building (erected)	168,905	
Site work (producer plant only)	1,395	
Total Construction Cost	737,719	
Engineering	73,772	
Interest During Construction	33,197	
Startup (60 days)	20,000	
Total Appropriation	864,688	2,704,688
Operating Cost Components,(d) $/year		
Electricity ($0.015/kwh)	6,620	
Water ($0.25/1000 gal)	10,640	
Chemicals (allowance)	1,000	
Supplies (allowance)	1,000	
Operating labor ($6/hr + fringes, G&A)	100,800	
Maintenance (2 percent of equipment)	11,348	

(a) Based on dry gas production of 65 scf/lb coal as given with cost data.

(b) Based on gas composition given with cost data, i.e., 39.3 mole percent $H_2 + CO + H_2S$.

(c) Chemical Engineering Plant Cost Index = 178.6.

(d) Operating time = 7000 hours/year.

Galusha gasifiers.(1) The production rate was 11,000 scfm of clean gas having a low heating value of 290 Btu/scf. Adjusting the gas composition from Table 9-2 to an oxygen-blown situation and adding 1.0 mole percent H_2S, the gas should contain about 86.9 percent $H_2 + CO + H_2S$. Thus, the production of $H_2 + CO + H_2S$ is 9,560 scfm. The investment quoted for this system was about $2.67 x 10^6 but did not include engineering and startup costs. The breakdown of this investment is shown in Table G-2. Based on the air-blown Wellman-Galusha information, the engineering cost was taken as 10 percent and the startup cost as $20,000. This made the total investment about $2.96 x 10^6.

Koppers-Totzek, Oxygen Blown

Two cost quotations were obtained from the Koppers Company in March, 1975, on systems involving a single two-headed Koppers-Totzek gasifier. The first quotation(2) involved a gasifier feeding 283.4 tons/day of Illinois No. 6 coal and producing 9,142 scfm of $H_2 + CO + H_2S$. However, this feed rate is less than the capacity of such a gasifier, which is about 440 tons/day of coal. For this coal, 440 tons/day would correspond to 14,190 scfm of $H_2 + CO + H_2S$. The total investment for this system was quoted as $13 x 10^6. The level of accuracy of this estimate was stated as ±25 percent. This investment includes the water wash step but not the oxygen plant.

The second quotation(1,3) involved a gasifier feeding 289.9 tons/day of Elkhorn No. 3 coal and producing 12,243 scfm of $H_2 + CO + H_2S$. This feed rate was stated to be 66 percent of the capacity of the gasifier (approximately 440 tons/day coal). Thus, for this coal the capacity of the gasifier corresponds to 18,550 scfm of $H_2 + CO + H_2S$. The total investment for this system was as follows:

Component	Cost, 10^6 $
Coal handling, pulverizing, drying, and feeding	2.5
Gasification, cooling, cleaning (water wash)	8.2
General items	3.4
	14.1

TABLE G-2. CAPITAL COSTS FOR WELLMAN-GALUSHA OXYGEN-BLOWN GASIFICATION SYSTEM

Component	Capital Cost, $
Site (allowance)	3,000
Coal handling	27,000
Gas producer building erected	410,000
Three 10' diameter gas producers	960,000
Heat recovery system	152,000
Tar removal system	29,000
Ductwork for clean up system	38,000
Compressor	144,000
Electrical	120,000
Painting (allowance)	36,000
Miscellaneous producer plant piping, valves, insulation (allowance)	120,000
Gas distribution lines (1000 lin. ft, 24" diam)	576,000
Fire protection	57,000
Total ex engineering and startup	2,672,000
Engineering (10 percent)	267,000
Startup	20,000
Total	2,959,000

In both the above quotations, the gas demand was less than the output of the normal-size Koppers-Totzek two-headed gasifier and yet one such gasifier was specified and costed as such. It may not be feasible to scale down this gasifier far below the normal size. In this case, any gas not needed for the reduction could be used to supply the energy needs of the FGD process and/or could be fed to the boilers. This extra energy is, of course, obtained at some cost.

A paper published by Koppers(4) gives investments for systems involving one or more four-headed Koppers-Totzek gasifiers. A four-headed gasifier can process about 590 tons/day of coal. These costs are not directly useful here because they include the H_2S removal facilities, but it is instructive to note that the size exponent for the investments is about 0.59. This is for scaling by using multiple gasifiers (based on 1 to 5 gasifiers) and, as mentioned above, does include the H_2S removal facilities.

Koppers-Totzek, Oxygen + Air Blown

A cost estimate was obtained on a Koppers-Totzek gasification system in which the gasifiers were to be blown with a 60/40 mixture of oxygen/air.(5) The system was to feed 1,853 tons/day of coal and to produce about 61,100 scfm of total gas, including about 48,400 scfm of $H_2 + CO + H_2S$. The June, 1974, investment estimate was $\$21.5 \times 10^6$, excluding the oxygen plant.

Riley-Morgan, Oxygen Blown

A quotation was obtained from the Riley-Stoker Corporation on a system involving three 10'6" diameter Riley-Morgan gasifiers.(1,6) The system was designed to feed 39,000 lb/hr of coal and to produce 21,250 scfm of dry gas (67,050 lb/hr). Using the clean, dry gas composition from Table 9-4 but adding 1.0 mole percent H_2S, the gas should contain 80.3 percent $H_2 + CO + H_2S$. Thus, the production of $H_2 + CO + H_2S$ is 17,060 scfm. The investment for the gasifiers and associated equipment was quoted as $\$2.9 \times 10^6$, but this does not include water washing of the gas.

Applied Technology Corporation, Air Blown

The Applied Technology Corporation (ATC) is marketing a two-stage gasifier essentially equivalent to the units which Wellman-Incandescent, Ltd., had previously offered. Many of the Wellman-Incandescent units are in use today and many have been operating for over 20 years. A quotation was obtained(7) on a system involving four 12-foot diameter gasifiers and having a total production capacity of 388 x 10^6 Btu/hr of hot, raw gas or 322 x 10^6 Btu/hr of cold, clean gas. The gas composition from the ATC gasifier should be similar to that from the Woodall-Duckham gasifier, since the latter is also a two-stage gasifier. A typical Woodall-Duckham composition(8) is:

Component	Mole Percent (Clean, dry)	
H_2	17.0	
CO	28.3	
CO_2	4.5	High heating value = 176 Btu/scf.
CH_4	3.0	
N_2	47.2	
	100.0	

The gas from the Wellman two-stage gasifier is stated to have a high heating value of about 175 Btu/scf.(9) Using this gas composition but adding 0.6 mole percent H_2S, the production of H_2 + CO + H_2S for this plant is calculated to be 13,900 scfm. The investment quoted was \$5.0 x 10^6, as shown in Table G-3.

Wilputte, Air Blown

Quotations were obtained from the Wilputte Corporation on systems involving 7 and 20 air-blown Wilputte gasifiers.(1,10) Each gasifier has a 10'4" inside diameter, feeds 30 tons/day of coal, and produces 2500 scfm of gas. A typical clean, dry gas composition is:

TABLE G-3. CAPITAL COSTS FOR APPLIED TECHNOLOGY CORPORATION GASIFICATION SYSTEM

Section	Estimated Capital Cost, 10^6\$
Coal handling and storage (on ground)	1.2
Gasifiers and auxiliaries(a)	2.7
Gas cooling and clean up(b)	1.1
Total	5.0

(a) Includes small package steam boiler. Does not include land, site preparation, and civil work for producer gas plants.

(b) Includes cooling towers and effluent water clean up.

Note: Above estimates include equipment, installation, buildings, and engineering.

Component	Mole Percent
H_2	16.6
CO	22.7
CO_2	5.9
CH_4	3.6
O_2	0.2
N_2	51.0
	100.0

High heating value = 170 Btu/scf.

After adding 0.6 mole percent H_2S, this gas contains 39.7 mole percent H_2 + CO + H_2S. The investments for the two systems are shown in Table G-4.

Consensus

Investment. As shown in Figure G-1, there is a fair amount of scatter in the investment data. If one were to draw a best fit line through all the data the slope would be considerably higher than the range of 0.6-0.7 which fits the size exponents of most chemical processing equipment. For the two sources for which two sizes were quoted, the calculated exponents are 0.71 (Wellman-Galusha) and 0.89 (Wilputte). As mentioned previously, a Koppers publication indicates an exponent of 0.59 for multiple gasifier systems. For correlating the data here, a size exponent of 0.7 was selected in order to stay within the bulk of chemical equipment data.

The two points for air-blown Wellman-Galusha systems and the point for the Riley-Morgan system were ignored because these costs did not include the gas-washing facilities. For the other seven points shown on Figure G-1, the cost was calculated for 10,000 scfm of H_2 + CO + H_2S using the 0.7 exponent. The average of these seven costs was \$7.03 x 10^6. Thus, the investment for a gasification system can be represented by the equation

$$\text{Investment, } 10^6\$ = 7.03(10^4 \text{ scfm } H_2 + CO + H_2S)^{0.7}.$$

It should be noted that 10,000 scfm of H_2 + CO + H_2S is close to the reductant requirement for a 1000-MW power plant under the assumptions of this study.

TABLE G-4. CAPITAL COSTS FOR WILPUTTE GASIFICATION SYSTEMS

	Seven Gasifiers	Twenty Gasifiers
Coal Input Rate, tons/day	210	600
Dry Gas Production Rate, scfm	17,500	50,000
Production of $H_2 + CO + H_2S$, scfm	6,950	19,850
Investment, 10^6\$		
Coal and ash handling	1.3	3.0
Gasifiers and waste heat boilers	2.8	8.0
Water treatment facilities	1.0	2.0
Total plant cost	5.1	13.0

This analysis did not disclose any general difference between the investments for air-blown and oxygen-blown systems, not considering the oxygen plant. One might expect the investment for air-blown systems to be higher because of the larger vessel sizes required, a difference which the cost of the oxygen plant would tend to offset, but if this is true it could not be detected in view of the scatter of these data. All that could be justified by the data was a single equation.

Operating Cost. The only source of operating cost data is that for the air-blown Wellman-Galusha system (Table G-1). These data do not include the water washing step, so this will have to be treated separately. Some of the other data sources gave operating cost data but included the H_2S removal operation in the data. The values from Table G-1, exclusive of maintenance, were used after being adjusted to the basis of this study. That is, the annual operating costs were adjusted proportionally to the annual operating time and the production rate of $H_2 + CO + H_2S$.

Residual Oil Gasification

Cost data on the Shell Gasification Process (SGP) for residual oil were taken from a paper by J. B. Plummer, et al, of the Shell Development Company.(11) The January, 1974, capital cost of an SGP unit processing 10,000 bbl/stream day of residual oil was given as $31 million for gasification with air and $16 million for gasification with oxygen. This includes the soot removal and recycle facilities but not H_2S removal. For gasification with air, the air compressor train is included. For gasification with oxygen, the oxygen plant is not included. These are installed process equipment costs including engineering and contingency. Updating these costs to 1975 (Chemical Engineering Plant Cost Index = 190) gives $\$39.1 \times 10^6$ for gasification with air and $\$20.2 \times 10^6$ for gasification with oxygen. The investment was taken as proportional to the 0.7 power of the oil feed rate.

Typical gas compositions and process requirements for the Shell process are given in Table G-5.

Oxygen Plants

The costs for oxygen plants were taken from a paper by J. T. Hugill.(12) The following investments and electricity consumptions were given.

	Oxygen Production Rate (T/D)		
	400	600	800
1974 Investment (10^3\$)			
Basic equipment	4.3	5.6	6.9
Erection	2.1	2.9	3.5
Total	6.4	8.5	10.4
Electricity Consumption (kwh/T O_2)	350	343	330

These investments indicate a size exponent of 0.70. After updating to 1975 (Chemical Engineering Plant Cost Index = 190), these investments can be represented by the equation

$$\text{Investment, } 10^6\$ = 0.1109(\text{T/D } O_2)^{0.7}.$$

In Figure G-2 these investments are compared with quotations obtained from the Koppers Company(2,3) and Mason and Hangar(1) as adjuncts to the gasification system costs previously discussed.

By plotting the electricity consumptions above, a value of 351 kwh/ton of O_2 was obtained for the range of oxygen plant sizes of interest in this study (150-300 T/D). These values apply for the production of 98 percent pure oxygen at slightly above atmospheric pressure.

According to Hugill, the 1974 cost of operating labor for 400-800 T/D O_2 plants is \$220,000 per year, this corresponds to about three operators per shift.

According to Shreve(13) the total cooling water requirement is 8,640 gal/ton of O_2. In a recirculating system with cooling towers only about 5 percent of this quantity would be required as makeup. According to Shreve, oxygen plants require 12.5 pounds of caustic soda (NaOH) per ton of O_2. The current cost of NaOH is about \$159/ton (\$150/ton of 73 percent Na_2O).

TABLE G-5. DATA ON SHELL RESIDUAL OIL GASIFICATION PROCESS

Gasification Agent		Oxygen	Air
Gas Composition, mole % dry basis			
H_2		47.1	14.5
CO		50.8	23.6
CO_2		1.2	1.0
CH_4		0.6	0.2
N_2		0.1	60.0
Ar		0.2	0.7
		100.0	100.0
Lower Heating Value of Gas, Btu/scf		298.6	116.6
Requirements Per 10^6 Btu of Gas LHV			
Item	Unit		
Residual oil	bbl	0.200	0.235
Naphtha	bbl	0.002	0.002
Steam	lb		
1350 psia		-81	-335
1275 psia, 925 F		122	224
65 psia		5.1	2.5
Electricity	kwh	2.80	1.96
Boiler feed water	gal	0	13.9
Total cooling water(a)	gal	1,590	1,860
scfm H_2 + CO for 10,000 B/D Residual Oil		113,800	96,600

(a) In a recirculating system only about 5 percent of this quantity will be required as makeup.

Source: Plummer, J. B., et al (Reference 11).

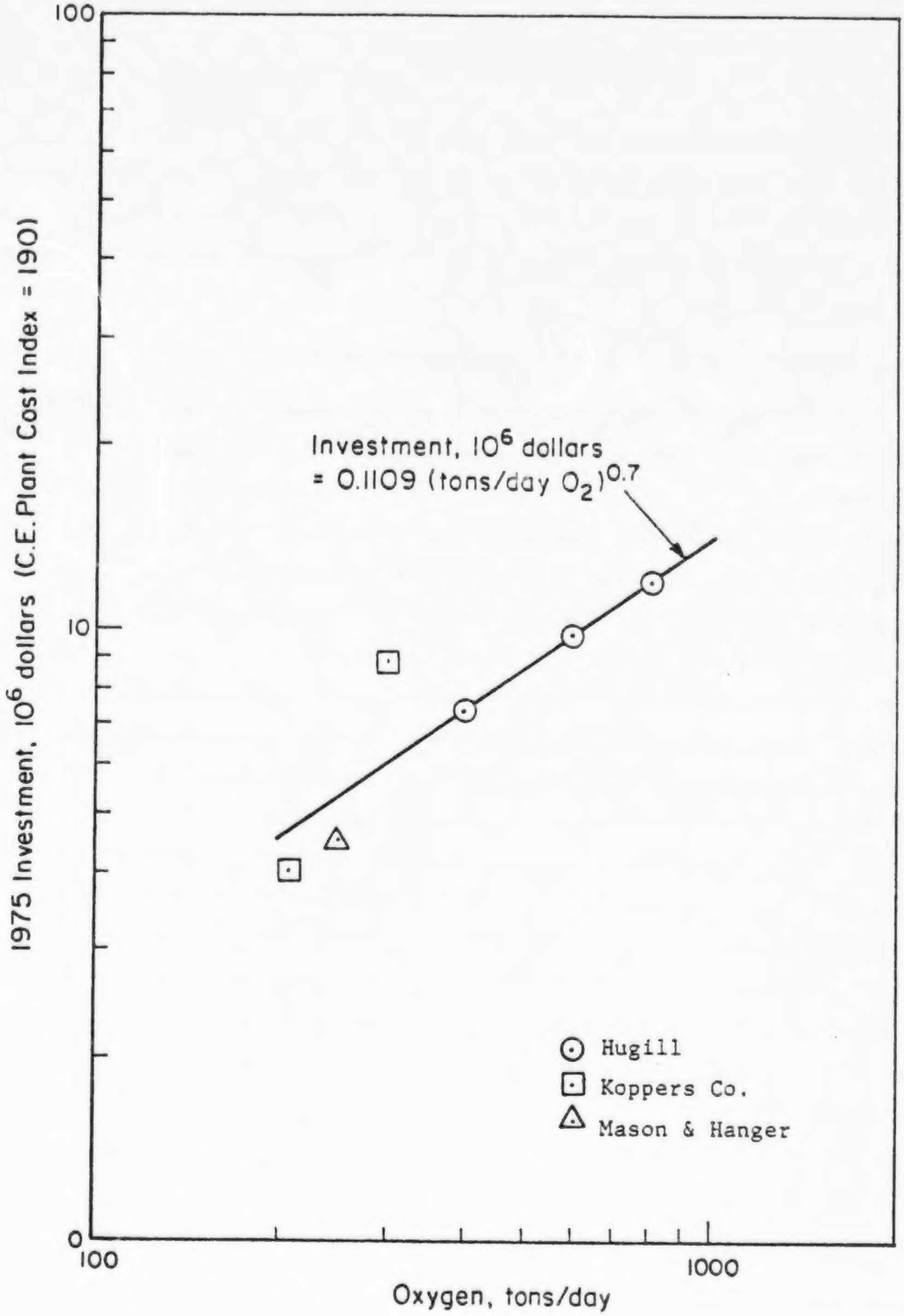


FIGURE G-2. INVESTMENT FOR OXYGEN PLANTS

Claus Sulfur Plants

Data on the investment for vapor-phase Claus sulfur plants are shown in Figure G-3. Probably the best source is a pair of quotations recently obtained from Ford, Bacon, and Davis, a leading vendor of Claus plants. The solid line on Figure G-3 is based on these data and is expressed by the equation

$$\text{Investment } (10^6\$) = 0.1354 \text{ (LT/D Claus sulfur)}^{0.6}.$$

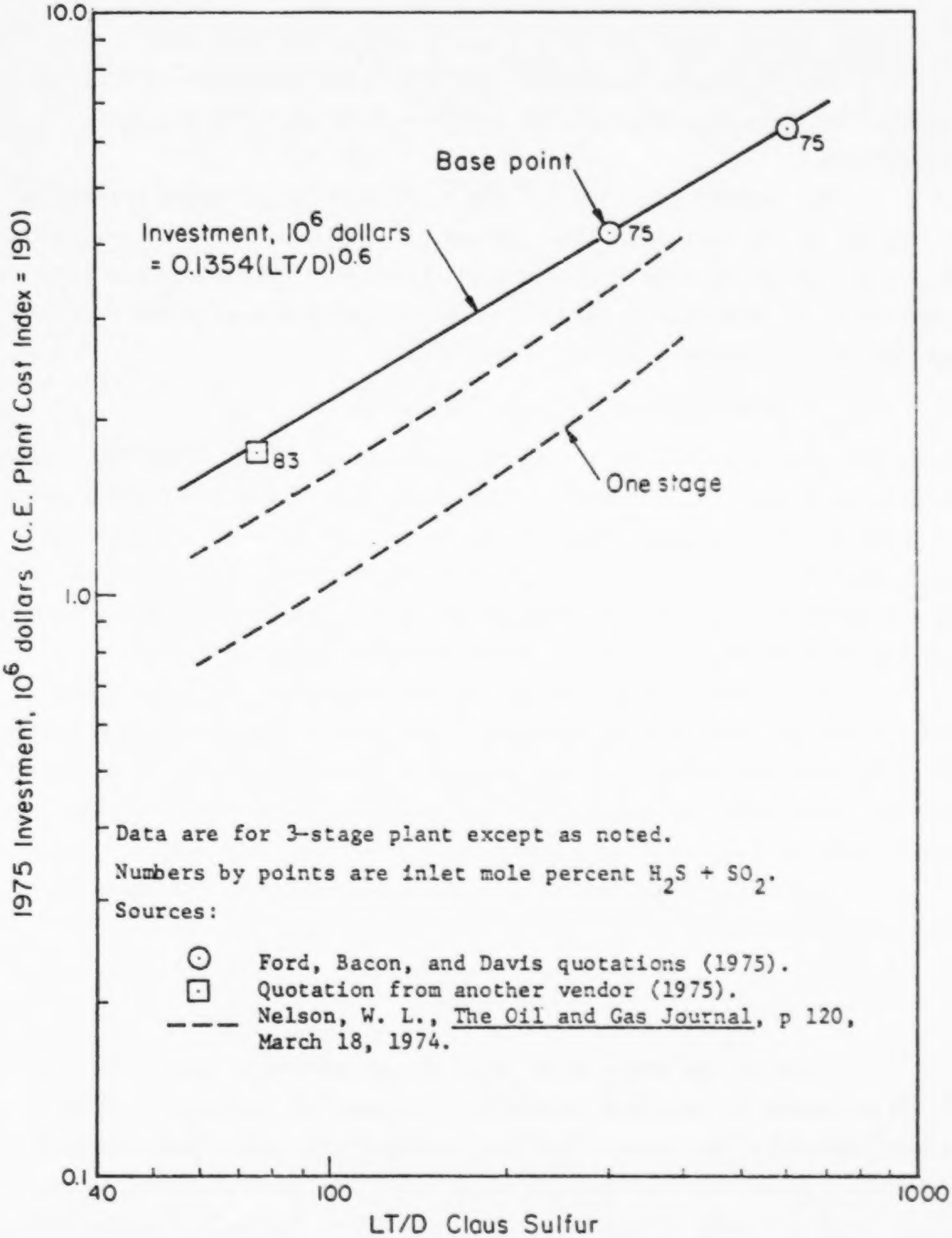
This is for a three-stage Claus plant with an inlet concentration of H_2S + SO_2 of about 75 mole percent. The sulfur recovery in such a plant is 95.5 to 96 percent.

Ford, Bacon, and Davis indicated that the investment for a two-stage plant is 8 to 10 percent less than that of a three-stage plant. The data of Nelson indicate that the investment for a one-stage plant is about 36 percent less than that of a three-stage plant.

The effect of the inlet gas concentration on the investment for Claus plants does not appear to be available in the open literature. However, information obtained from the Allied Chemical Corporation(14) states that "Sizing of equipment in a Claus unit is primarily a function of gas volume. Claus converter sizing (packed bed reactor) is based on contact time and, thus, gas velocity and volume. The major portion of the heat load in the sulfur condensers is sensible heat of the gas and thus a volume flow function. Incinerator design is based on retention time and thus a volume flow function." It would, therefore, appear to be reasonable to assume that the investment varies with the 0.6 power of the inlet gas volume.

Based on information from vendors, the operating requirements for Claus plants include the following:

Item	Amount	
Electricity	50 kwh/LT sulfur	
Boiler feed water	800 gal/LT sulfur	
Activated alumina	0.4 lb/LT sulfur	(Cost = 14¢/lb)
Steam produced	600 lb/LT sulfur.	



Data are for 3-stage plant except as noted.

Numbers by points are inlet mole percent $H_2S + SO_2$.

Sources:

- ⊙ Ford, Bacon, and Davis quotations (1975).
- ⊡ Quotation from another vendor (1975).
- — — — Nelson, W. L., The Oil and Gas Journal, p 120, March 18, 1974.

FIGURE G-3. INVESTMENT FOR CLAUS SULFUR PLANTS

Allied Chemical Reduction Process

For the reduction systems for Type A FGD processes, the Allied Chemical SO_2 Reduction process was used as a base case for economic comparisons.

The capital cost for the Allied process is primarily a function of the gas volume processed and secondarily of the inlet SO_2 concentration (i.e., the amount of sulfur processed). Based on a plot contained in a paper by W. D. Hunter of Allied,(15) the following equation was derived for the on site (battery limits) investment:

$$\text{Investment, } (10^6\$) = A\ (\text{megawatts capacity})^B$$

where the constants A and B are shown as functions of the inlet SO_2 concentration in Figure G-4. In spite of the variation of the constants A and B with inlet SO_2 concentration, the above equation should be considered valid only for coal containing about 3.5 weight percent sulfur, since this is the basis for the data on which it is based. The constant A has been updated to 1975 using the Chemical Engineering Plant Cost Index.

An important component of the operating cost for the process is the natural gas used as the reductant. The natural gas consumption varies directly with the quantity of SO_2 reduced. Based on a figure presented by Hunter, the natural gas requirement for a 1000-MW power plant burning 3.5 weight percent S coal was calculated to be 4.95×10^6 scf/day.

The other components of the operating cost were estimated from published information(16,17) and process calculations.

Ductwork Costs

Much of the ductwork involved in the reduction system for Type A FGD processes is included in the cost estimate for the gasification system and the Claus plant. However, there is some additional ductwork connecting these major processing steps which must be considered separately. It is very difficult to estimate these additional ductwork costs because they are in reality very situation-specific. However, even a rough estimate is better than none at all.

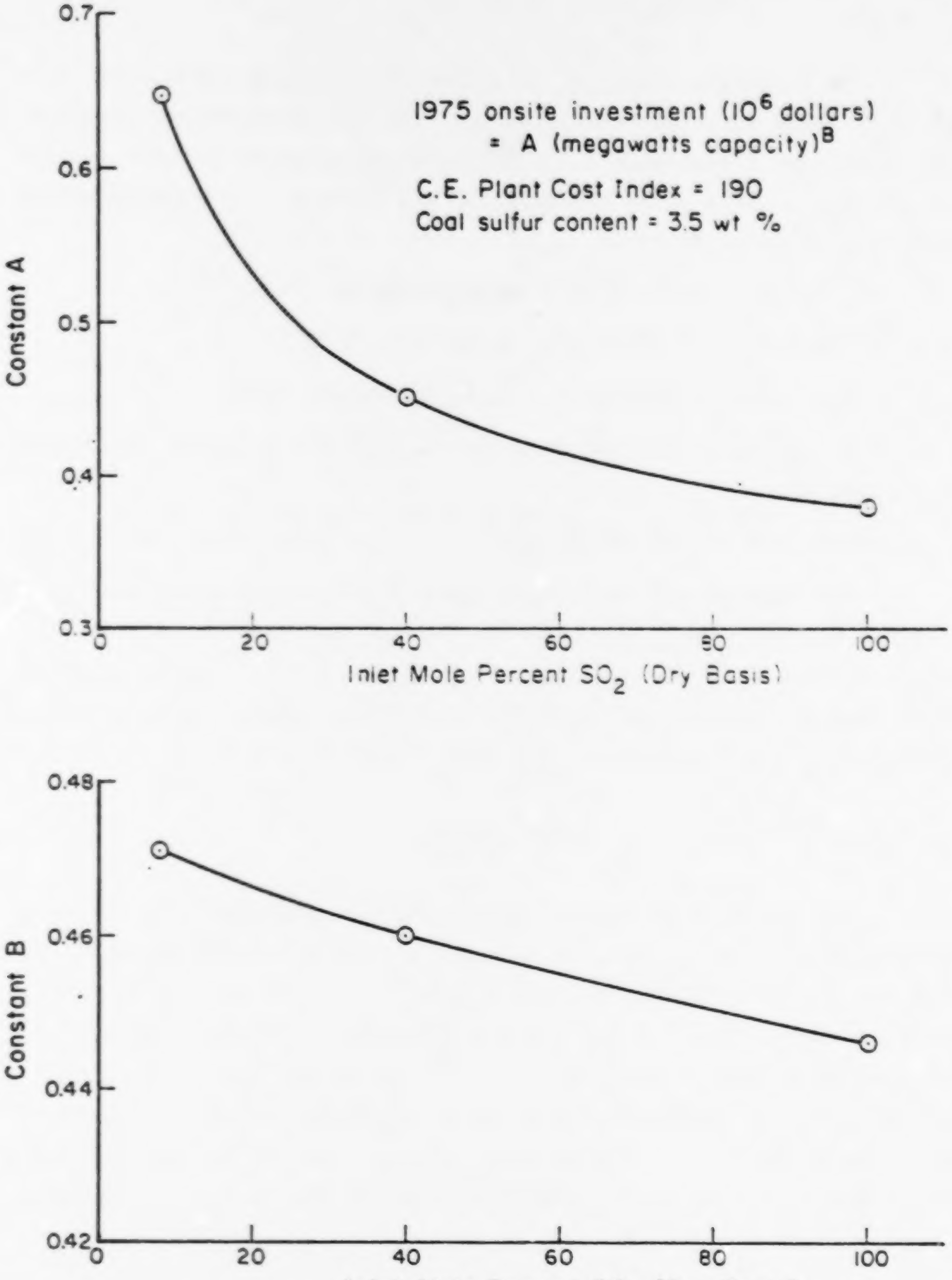


FIGURE G-4. CONSTANTS IN INVESTMENT FUNCTION, ALLIED SO_2 REDUCTION PROCESS

The materials and labor costs for ductwork were taken from Mills.(18) These costs are expressed in terms of the equivalent diameter of the duct, even though such ducts are often rectangular in cross section. After updating to 1975 using the Marshall and Stevens Index, the materials cost for carbon steel ducts is

$$\text{Materials cost, \$/ft} = 14.49 \text{ (diameter, feet)}^{0.812}.$$

At a total labor cost of $10/hour, the labor cost is

$$\text{Labor cost, \$/connection} = 41.29 \text{ (diameter, feet)}^{1.045}.$$

For a linear gas velocity of 20 ft/sec at atmospheric pressure, the equivalent diameter is

$$\text{Diameter, feet} = 0.003495 \sqrt{\text{(Flow rate, lb moles/hr)(Temp, R)}}.$$

The calculations made using these equations are summarized in Tables G-6 and G-7. Note that only the streams which are not part of the gasification system or the Claus plant are included here. These estimates must be regarded as order-of-magnitude costs only. Their magnitude is such that they have little effect on the total system cost anyway.

Blower Costs

The reduction system for Type A FGD processes requires several blowers which are not included in the cost estimates for the gasification system and the Claus plant. The estimation of the capital cost of these blowers is shown in Table G-8. The equipment cost, including the blower, motor, and drive, was taken from Mills.(18) To obtain the total capital cost, the equipment cost was multiplied by a "module factor" from Guthrie,(19) which reflects the cost of installation, foundations, electrical and piping hookups, and other facilities associated with the basic piece of equipment.

TABLE G-6. ESTIMATION OF INCREMENTAL DUCTWORK COSTS FOR AN OXYGEN-BLOWN GASIFIER

Unit costs ($/ft and $/connection) are for uninsulated carbon steel ducts
Values are for 1000-MW plant except as indicated

		85% SO_2 Case			25% SO_2 Case		
Stream Number[(a)]	Temp, R	Diameter, ft	Material, $/ft	Labor, $/conn	Diameter, ft	Material, $/ft	Labor, $/conn
5	540	0.56	9.1	23	0.56	9.1	23
7	1110	5.60	58.7	250	5.60	58.7	250
8	540	2.49	30.4	107	4.59	49.9	203
9	1010	5.54	58.2	247	7.65	75.6	346
10	540	2.14	26.9	91	2.14	26.9	91
11	760	5.33	56.4	237	7.02	70.5	316
Total Cost, 10^3\$[(b)]							
1000 MW			16.1	13.0		19.6	16.6
500 MW			12.2	9.1		14.8	11.6

(a) Refers to Figure 13-1 of the text.

(b) Includes 10 ft and 2 connections for stream 10, 50 ft and 8 connections for all other streams.

NOTE: In total costs, values for high-temperature streams (>540 R) reflect 60 percent increase in material cost for alloy steel and insulation, 100 percent increase in labor cost for insulation.

TABLE G-7. ESTIMATION OF INCREMENTAL DUCTWORK COSTS FOR AN AIR-BLOWN GASIFIER

Unit costs ($/ft and $/connection) are for uninsulated carbon steel ducts
Values are for 1000-MW plant except as indicated

		85% SO_2 Case			25% SO_2 Case		
Stream Number(a)	Temp, R	Diameter, ft	Material, $/ft	Labor, $/conn	Diameter, ft	Material, $/ft	Labor, $/conn
4	540	1.98	25.2	84	1.98	25.2	84
5	1110	8.64	83.5	393	8.64	83.5	393
6	540	2.49	30.4	107	4.59	49.9	203
7	1010	8.38	81.4	381	9.90	93.2	453
8	540	3.42	39.3	149	3.42	39.3	149
9	760	8.25	80.4	375	9.44	89.7	431
Total Cost, $10^3$$(b)							
1000 MW			21.8	19.7		24.5	22.5
500 MW			16.5	13.7		18.5	15.7

(a) Refers to Figure 13-3 of the text.

(b) Includes 10 ft and 2 connections for streams 4 and 8, 50 ft and 8 connections for all other streams.

NOTE: In total costs, values for high-temperature streams (>540 R) reflect 60 percent increase in material cost for alloy steel and insulation, 100 percent increase in labor cost for insulation.

TABLE G-8. INVESTMENT AND POWER REQUIREMENTS FOR BLOWERS

1000-MW Power Plant

	Oxygen-Blown Gasifier Case		Air-Blown Gasifier Case	
	85% SO_2 Case	25% SO_2 Case	85% SO_2 Case	25% SO_2 Case
Equipment Cost, $10^3\$^{(a)}$				
Air to reheat burner			2.18	2.18
SO_2-rich stream	2.84	7.47	2.84	7.47
Cleaned reducing gas$^{(b)}$	11.40	11.40	26.81	26.81
Air to tail gas incin.	2.39	2.39	4.58	4.58
Total	16.63	21.26	36.41	41.04
Total Installed Cost of Blower & Associated Facilities, $10^3\$^{(c)}$	51.7	66.1	113.2	127.6
Horsepower$^{(d)}$				
Air to reheat burner			12	12
SO_2-rich stream	18	63	18	63
Cleaned reducing gas	93	93	223	223
Air to tail gas incin	14	14	35	35
Total	125	170	288	333

(a) From Mills (Reference 18).

(b) Two blowers for oxygen-blown case, four blowers for air-blown case.

(c) Based on module factor of 3.108 for compressors from Guthrie (Reference 19).

(d) Based on a pressure drop of 0.4 psi.

H_2S Generation Facilities

The costs for the H_2S generation facility required for the Type B FGD processes were based on a quotation obtained from C & I/Girdler, Inc., for that purpose.(20) This information is presented in Table G-9. For a 1000-MW power plant fired with 3.5 percent sulfur coal, a Type B FGD process will require 725 tons/day of H_2S. Girdler pointed out that they do not have accurate cost data for such a large plant, since the largest H_2S plant they have built to date has a capacity of 60 tons/day.

The Girdler process is designed to utilize "bright" sulfur and not "dark" sulfur. About 10 percent of the sulfur fed to the plant must be blown down from the system. This sulfur is dark but is suitable for use in the manufacture of sulfuric acid.

Reductant Gas Upgrading Facilities

Prior to its use for H_2S generation, the coal gas must be upgraded, through CO shifting and acid gas (CO_2) removal, to increase the concentration of hydrogen. The investments for these facilities were based on data obtained from the U.S. Bureau of Mines(21) on making hydrogen from coal gas. These data were adjusted for differences in the capacity and operating pressure. Table G-10 shows the resulting investments for these facilities for a 1000-MW power plant. Each segment of the processing sequence includes all the equipment, such as pumps and heat exchangers, associated with the operation involved.

TABLE G-9. DATA ON GIRDLER H_2S GENERATION PROCESS

	Case A	Case B
Plant Capacity	725 T/D	725 T/D
No. of Trains	3	4
Capacity/Train	242 T/D	181 T/D
Approximate Installed Cost	$9,000,000	$9,700,000

Product Delivery Conditions

Pressure	80 psig
Temperature	54 C (130 F)
H_2O	Same as H_2 feed

Feed Gas Conditions

Pressure	140 psig
Temperature	38 C (100 F)

Feed Gas Analysis, mole percent

H_2	90.5
CO	1.91
CO_2	1.89
CH_4	0.12
N_2	1.03
A	0.46
H_2O	4.09
	100.00

Approximate Product Analysis, mole percent

H_2	2.0
H_2S	88.5
CO	0.23
COS	1.7
CO_2	1.9
CH_4	0.08
CS_2	0.04
N_2	1.0
A	0.45
H_2O	4.1
	100.00

TABLE G-9. (Continued)

Estimated Utility Requirements	Quantity/Ton H_2S
Feed gas	25,000 scf
Bright sulfur (liquid at slight positive head)	2,160 lb
Electric power (440 V-3 PH-60 Cy)	15 kwh
Steam for jackets (40 psig)	700 lb
Cooling water (32 C max temp)	5,500 gal

TABLE G-10. INVESTMENT DATA ON REDUCING GAS UPGRADING FACILITIES

Facility	1975 Investment, 10^6\$	Items Included
Shift converter 1	0.295	Converter, feed gas heater, feed water pump
Waste heat recovery	1.885	Waste heat boiler, boiler feed pump, cooler, knockout drum
Acid gas removal 1(a)	5.047	Absorber, regenerator, reboiler, solution pumps, solution cooler, acid gas cooler and knockout drum, clean gas cooler and knockout drum, iron oxide tower, char tower, solution storage and mixing tanks, centrifuge, makeup pump
Shift converter 2	0.466	Converter, feed gas heater, feed water pump, aftercooler, knockout drum
Acid gas removal 2	1.773	Absorber, regenerator, reboiler, solution pumps, solution cooler, acid gas cooler and knockout drum, clean gas cooler and knockout drum, solution storage and mixing tanks, centrifuge, makeup pump
Total	9.466	

(a) Two trains.

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(13) Shreve, R. N., Chemical Process Industries, 3d Edition, McGraw-Hill Book Company, 1967.

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(18) Mills, H. E., "Costs of Process Equipment", Chemical Engineering, p 133, March 16, 1964.

(19) Guthrie, K. M., "Capital Cost Estimating", Chemical Engineering, p 114, March 24, 1969.

(20) Letter to Mr. Paul Choi (BCL) from Mr. Donald M. Hess (C & I/Girdler, Inc.), November 20, 1975.

(21) Personal communication between BCL and the U.S. Bureau of Mines, Morgantown, West Virginia, 1975.

APPENDIX H

CONVERSION FACTORS

APPENDIX H

CONVERSION FACTORS

To Convert (English)	To (Metric)	Multiply By
atmospheres	kilograms/m^2	10,333
barrels (42 gal)	liters	159.0
Btu	kilocalories	0.2530
Btu/ft^3	kilocalories/m^3	8.935
Btu/lb	calories/gram	0.5578
ft	meters	0.3048
ft^3 (cubic feet)	m^3 (cubic meters)	0.02832
gallons	liters	3.785
grains	grams	0.06480
grains/ft^3	grams/m^3	2.288
in.	cm	2.540
in. H_2O	kilograms/m^2	25.40
long ton (2240 lb)	metric ton (2205 lb)	1.016
pounds	grams	453.6
pound-moles	gram-moles	453.6
pounds/in.^{2} (psi)	kilograms/m^2	703.1
ton, short (2000 lb)	metric ton (2205 lb)	0.9070

$$\text{Temperature in C} = \frac{(\text{Temperature in F}) - 32}{1.8}$$